Emerging Organic Contaminants in Effluent, Applied Soils and Receiving Shallow Groundwater in the Canterbury Region

A thesis

Submitted in partial fulfilment

of the requirements for the degree

of

Masters in Environmental Science

at the

University of Canterbury

By

Rebecca van der Krogt

Table of Contents

Acknowledgements

I would like to acknowledge and thank my supervisors, Associate Professor Sally Gaw for her support and encouragement when the work got tough, her patience and hands on teaching approach which helped me get started on what was initially very foreign. Further thanks to my co-supervisors Murray Close (ESR) and Dr Grant Northcott (Northcott Research Consultants) for their patience and advice during my thesis. I thank the Brian Mason Scientific trust for the financial support for my project and the Evans fund for financial support towards travel expenses. I would like to thank Lisa Scott (Environment Canterbury) for her help and advice with the selection of sites and for putting me in contact with the relevant people.

I would like to thank all the people who helped organise and collect my groundwater, soil and effluent samples, Euan Cox, Donald Boyd, Alex Smith (Ashburton District Council) David Perry, Garry Harris, Rick (Hurunui District Council), Daniella Murugesh, Ian Baker (Christchurch City Council), David Evans and Ross Cressy (Environment Canterbury).

I would also like to thank those who helped me with special training in the lab and organising equipment and chemicals required. Matt Polson for maintenance and use of the GC-MS, John Revell for calibration and use of field meters, Rob Stainthorpe for clean room training, Michael Sandridge for training on the TOC analyser, Gill Ellis and Laurie Anderson for ordering of special chemicals and supplies. I would also like to thank the workshop staff, Danny Leonard and Robert McGregor for helping fix lab and field equipment.

Thanks to everyone in the Chemistry department especially the Environmental Chemistry Group for your encouragement and support, coffee breaks, ice cream trips and making the whole process a lot more enjoyable.

Finally, a huge thank you to all my friends and family, Mum, Dad and Jarrod who helped me survive the past five years of study especially my final year. A massive thanks to mum for giving up her weekends bringing me dinners and supervising me at uni so that I could work late, I couldn’t have done it without you. And a special thanks to Martin for supporting me and making this last year possible.

Abstract

Emerging organic contaminants (EOCs), are of increasing concern, they are defined as compounds which are not necessarily new but are of importance due to their potential ecological and environmental effects. They are only recently discovered in the environment due to analytical advancements. This was the first study to investigate the presence of EOCs in shallow groundwater in New Zealand. This thesis investigated the presence of EOCs in groundwater and in potential sources to groundwater including dairy effluent and wastewater treatment plant effluent and soils receiving these types of effluents.

To determine concentrations of EOCs in soil, effluent and the particulate phase of both groundwater and effluent, a novel method was developed. This method involved extraction by ultrasonication and clean-up via dispersive solid phase extraction enhanced matrix removal. The developed method had good recoveries for most analytes, with recoveries between 70%-137% for soil, 62%-189% for effluent and 66%-121% for particulates. This newly developed method was applied to six soil samples and five effluent samples collected from within the Canterbury region. Four of the twenty-five target compounds were quantified in the soil samples including methylparaben, methyltriclosan, ethinylestradiol (EE2) and androstenedione. Concentrations (0.8 -152.5μg/kg) of EOCs in soil were of the same magnitude but at a greater concentration compared to the overseas literature. Eleven of the twenty-five target compounds were detected in the effluent samples including methylparaben, ethylparaben, OPP, propylparaben, 4MBC, BP3, triclosan, BP1, BPA, E3 and testosterone. Concentrations (5.5-246.8 ng/L) detected in effluent were comparable to international effluent concentrations.

To assess Canterbury groundwater for contamination from EOCs, 18 shallow groundwater wells <25 meters in depth were selected from across the Canterbury region. Wells were selected based on the likelihood of contamination, expert advice and site accessibility. The wells were sampled twice, once during spring and once during summer. A previously developed and validated method was used for the extraction of the dissolved phase of analytes from groundwater with good recoveries ranging from ~70%-120%. The maximum concentrations of target analytes

detected in the dissolved phase of groundwater ranged from below the limit of detection to 453.5 ng/L. Most of the concentrations detected were comparable to the lower end of detections in overseas countries. There were almost an equal number of EOC detections in the dissolved phase of groundwater across both seasons. However, the concentration of target analytes were significantly greater during spring. The suspended particulate phase of the groundwater samples was also analysed for the same suite of EOCs. Unlike the dissolved phase there was an obvious seasonal trend for the particulate phase with the majority of detections made during spring.

The maximum concentrations of EOCs detected in the dissolved phase of groundwater were used in an ecological and human health risk assessment. Hazard quotient values were calculated separately for ecological and human health risk. Of the twelve compounds quantified in groundwater, eleven had ecological hazard quotients well below 1 and therefore indicative of an extremely low level of risk. However, OP was found to have an ecological hazard quotient of 1.5 indicating a medium level of risk and thus requires further investigation. All human health hazard quotients values were well below 1 and therefore indicative of minimal risk towards humans. Due to the current concentrations of EOCS in groundwater representing a low level of risk, inclusion of these compounds into monitoring programmes may not be necessary at this stage.

Abbreviations

4-MBC - 4-methylbenzylidene camphor

ACN - Acetonitrile

BP-1 - Benzophenone-1

BP-3 - Benzophenone-3

BPA - Bisphenol A

bParaben - Butyl paraben

DCM - Dichloromethane

DOM - Dissolved organic matter

d.w. - dry weight

EDCs- Endocrine disrupting compounds

eParaben- Ethyl paraben

E1- Estrone

E2 - 17β-estradiol

E3 - Estriol

EE2 - 17α-ethinyl estradiol

GC-MS - Gas chromatography mass spectrometry

LOD - Limits of Detection

LOQ - Limits of Quantification

MeOH- Methanol

MQ - MilliQ

mParaben - Methyl paraben

NP - 4-*n*-nonylphenol

OMC - 2-ethylhexyl-*p*-methoxycinnamate

OP - 4-t-octylphenol

PCBs - Polychlorinated biphenyls

PCPs - Personal care products

pParaben - Propyl paraben

SPE - Solid phase extraction

UV light - Ultraviolet light

WWTP - Wastewater treatment plant

List of Figures

List of Tables

List of Equations

CHAPTER ONE

INTRODUCTION

1 Introduction

1.1 Background

There is an increasing concern regarding contamination of groundwater by emerging organic contaminants (EOCs). An EOC as defined by the US Geological Survey is; "Any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected ecological and/or human health effects." Emerging organic contaminants include human pharmaceuticals, veterinary medicines, nanomaterials, personal care products and biomolecules excreted by humans and animals[1]. During the last decade, there has been an increase in the release of EOCs to the environment due to changes in the socio-economic structure of society. Emerging organic contaminants are a potential risk to the environment due to the high quantities routinely released and their generally low biodegradability[2]. EOCs are often described as pseudo persistent due to their continuous release, concentrations in the environment can remain constant despite often having short half-lives. These compounds are not routinely monitored as they are often not included in environmental legislation and their environmental fate is not always well understood[3]. There are no previous studies analysing groundwater in New Zealand for EOCs and there are limited studies on EOCs in the New Zealand environment.

1.2 Groundwater

Groundwater is defined as the water situated below the water table within interconnected pores [4], and can be defined as an unconfined or confined aquifer [5]. Unconfined aquifers allow water to seep from the ground surface directly above the aquifer, whereas confined aquifers have an impermeable layer of dirt or rock which prevents water from seeping into the aquifer [5].

The main source of recharge to groundwater occurs during winter in the months from June – August via percolation of rainwater through porous soils [6]. Beneath the porous soil rainwater travels through two zones the unsaturated and saturated zone (Figure 1.1). Firstly, rainwater flows through the unsaturated zone, this zone contains water and air [7]. It can be divided up into three parts: the soil zone, intermediate zone and the capillary fringe. Once the water passes

through these zones it reaches the saturated zone [8]. The saturated zone is filled with interconnected openings in the ground full of water. This water is known as “groundwater”. Groundwater can either be pumped to the surface or naturally flow from artesian springs due to pressure [9].

Groundwater and surface water systems are interlinked, meaning that any events occurring at the surface can have an impact on the groundwater beneath [9]. Compared to surface water, groundwater pollution by emerging contaminants is less well characterised. Groundwater contamination can occur through the application of biosolids to agricultural land, waste disposal, leakage from septic tanks and sewer networks, and urban and rural stormwater run-off [10] [11]. Numerous case studies in the USA have reported EOCs in groundwater impacted by septic tanks [12] [13] [14]. Veterinary medicines have also become a growing concern in groundwater in intensive farming regions in the USA, parts of Europe and Asia [15] [16] [17].

Groundwater is of great importance as it is often used as a source of untreated drinking water and is also a source for irrigation to land. When compared with surface water environments, groundwater often has a high degree of protection from contamination [11]. Nevertheless, emerging contaminants have been reported in groundwater in trace concentrations in many recent international studies [18] [19] [20].

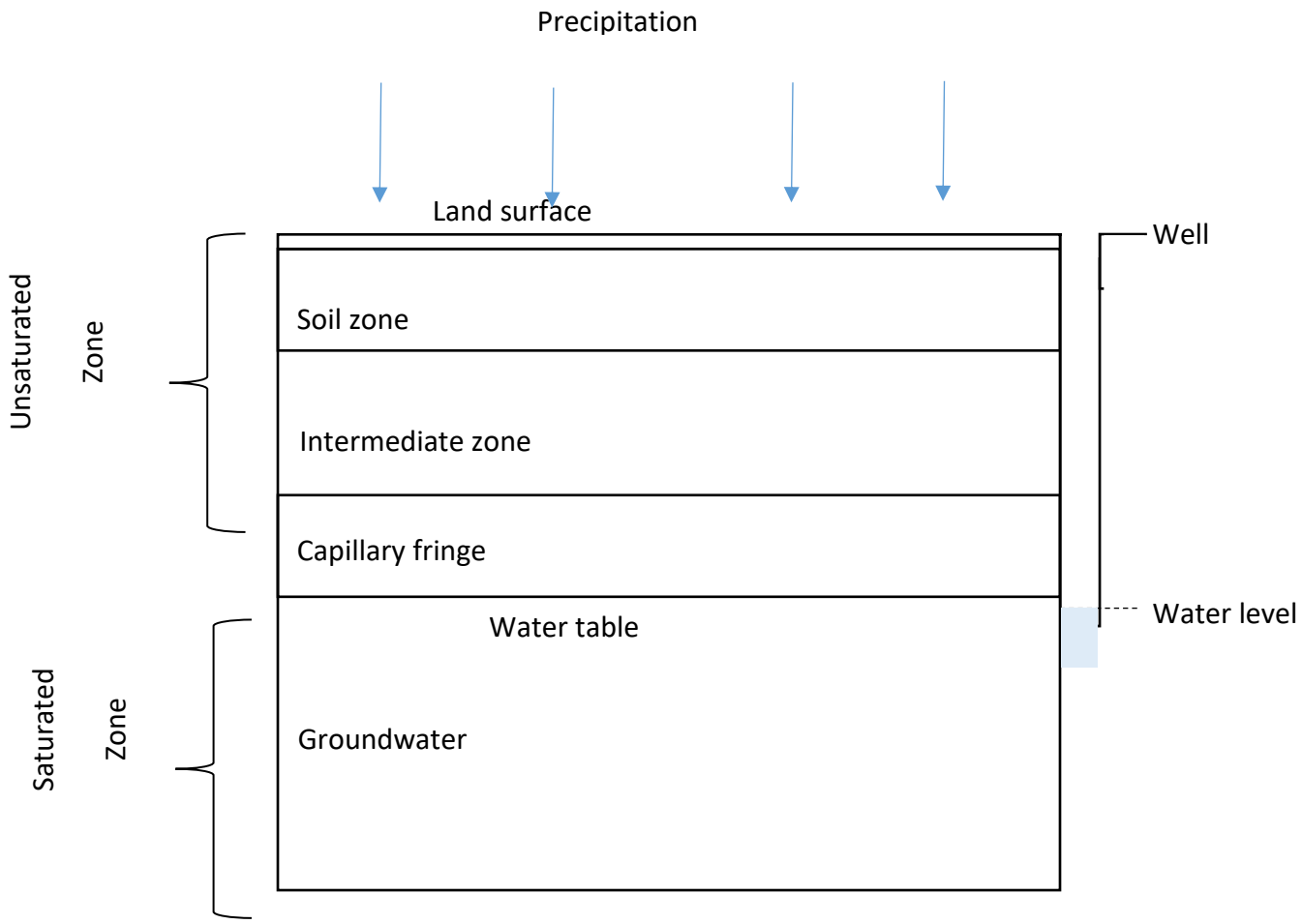


Figure 1.1: Diagram showing precipitation as a source of recharge and the zones it travels through to reach groundwater

1.2.1 Groundwater in Canterbury

Christchurch, the largest city within the Canterbury region, has some of the best quality groundwater in the world [21]. The aquifers beneath Canterbury supply 100% of the city's drinking water at an extraction rate of approximately 7000m^3/h [22]. The age of the groundwater depends on the depth of the aquifer. Carbon dating has been used to determine the age of the groundwater[23]. The upper aquifer of less than 50 metres depth is predicted to be 0-10 years of age whereas the much deeper aquifer with a depth greater than 150m is approximately 800 years old [23]. Groundwater in Canterbury is the dominant source of municipal water supply, irrigation, maintaining base river flows and aquatic habitats.

There are a variety of different sources within the region that have the potential to cause groundwater contamination. Within the Canterbury region dairy farming is a dominant land use, wastewater from farming sites are a potential source of veterinary pharmaceuticals and steroid hormone contamination to groundwater [17]. Other potential sources within the Canterbury region include irrigation of wastewater to land, and leakage from landfill and sewage systems [24].

In Canterbury, water resources are under the jurisdiction of the Canterbury Regional Council (ECan) under the Resources Management Act (RMA) and the abstraction of water requires a resource consent. Groundwater in Canterbury is under increasing pressure due to changes in climate, infrastructure and farming [25]. In recent years, much of the arable and livestock farming in the region has been converted to dairy farming [26]. This has put a huge demand on water resources within the region due to dairy farming requiring intensive use of water. Over allocation and exploitation of groundwater results in degradation of groundwater quality [27].

1.2.2 Existing Groundwater Monitoring Programmes in Canterbury

Each year in spring, in the months from September to December, Environment Canterbury collects groundwater samples from wells across the Canterbury region. The samples are analysed for a range of water quality parameters [28]. Nitrate nitrogen and faecal coliforms are the most commonly assessed health related contaminants with established maximum allowable values for drinking water.

At present Environment Canterbury, do not analyse for emerging organic contaminants, on occasion they monitor pesticides and hydrocarbons in some parts of the region [29]. Every four years since 1990 the Institute of Environmental Science and Research (ESR) has coordinated a national survey of pesticides in New Zealand groundwater. The most recent survey was undertaken in 2014 and was the seventh consecutive survey. Over the years this survey has been carried out there has been no increasing or decreasing trend in the levels of pesticides detected, in each national survey most wells have detected no pesticides and the concentrations of those detected are low [30], no pesticides were detected in the Canterbury region for the most recent pesticide survey undertaken in 2014 [31].There has been a link shown between higher nitrate concentration and pesticide detections [32].

1.3 Emerging Organic Contaminants

1.3.1 Sources of EOCS to Groundwater

The major sources of EOCs to groundwater are summarised below and in Figure 1.2.

Sewage

Sewage contains a wide variety of EOCs including pharmaceuticals, illicit drugs and compounds present in personal care products such as uv-filters and preservatives, household chemicals and industrial chemicals. These compounds are not fully removed during current waste water treatment plant processes [33]. The treated effluent is then disposed to land where it can infiltrate groundwater, or it is sometimes released into rivers where it is able to reach groundwater via groundwater surface water exchange. Leakage from septic tanks and municipal sewer pipes can also result in contamination of ground and surface waters by EOCs[34]. In New Zealand it is common practice for wastewater to be irrigated to land and biosolid material to be recycled and applied to land as a fertiliser [35]. This practice can cause migration of EOCs through the soil enabling the contamination of groundwater.

Landfill leachate

Landfill leachate is also likely to contain a wide variety of EOCs including pharmaceuticals, personal care product ingredients and industrial compounds. Landfills are often lined despite this contamination of groundwater is still observed. Examples of EOCs measured in landfill leachates include parabens, uv-filters, phenols (OP, NP, BPA and triclosan), pharmaceuticals and hormones [36].

Agriculture

The agricultural industry is an important industry for the New Zealand economy. Agriculture is a source of veterinary medicines, steroid hormones and industrial compounds [37]. The use of veterinary medicines is thought to be less in New Zealand compared to overseas countries [24]. Waste from dairy cows are either deposited directly to land or washed down from the dairy shed where it is often stored in an onsite waste lagoon. From the lagoon it is usually irrigated to land where EOCs migrate through soil to groundwater.

Stormwater

Stormwater contains a variety of EOCs due to vehicles, building materials, waste disposed of down stormwater drains and leaking sewers [38 39]. There is limited literature investigating EOCs in stormwater, classes that have been detected to date include alkylphenols, flame retardants, musk fragrances, phthalates, plasticisers and pharmaceuticals [39]

Recreational Activities

Recreational activities such as swimming can cause contamination of water bodies through personal care products washed off the skin such as sunscreens. Higher concentrations of uv-filters have been reported in sampled waters during summer [40].

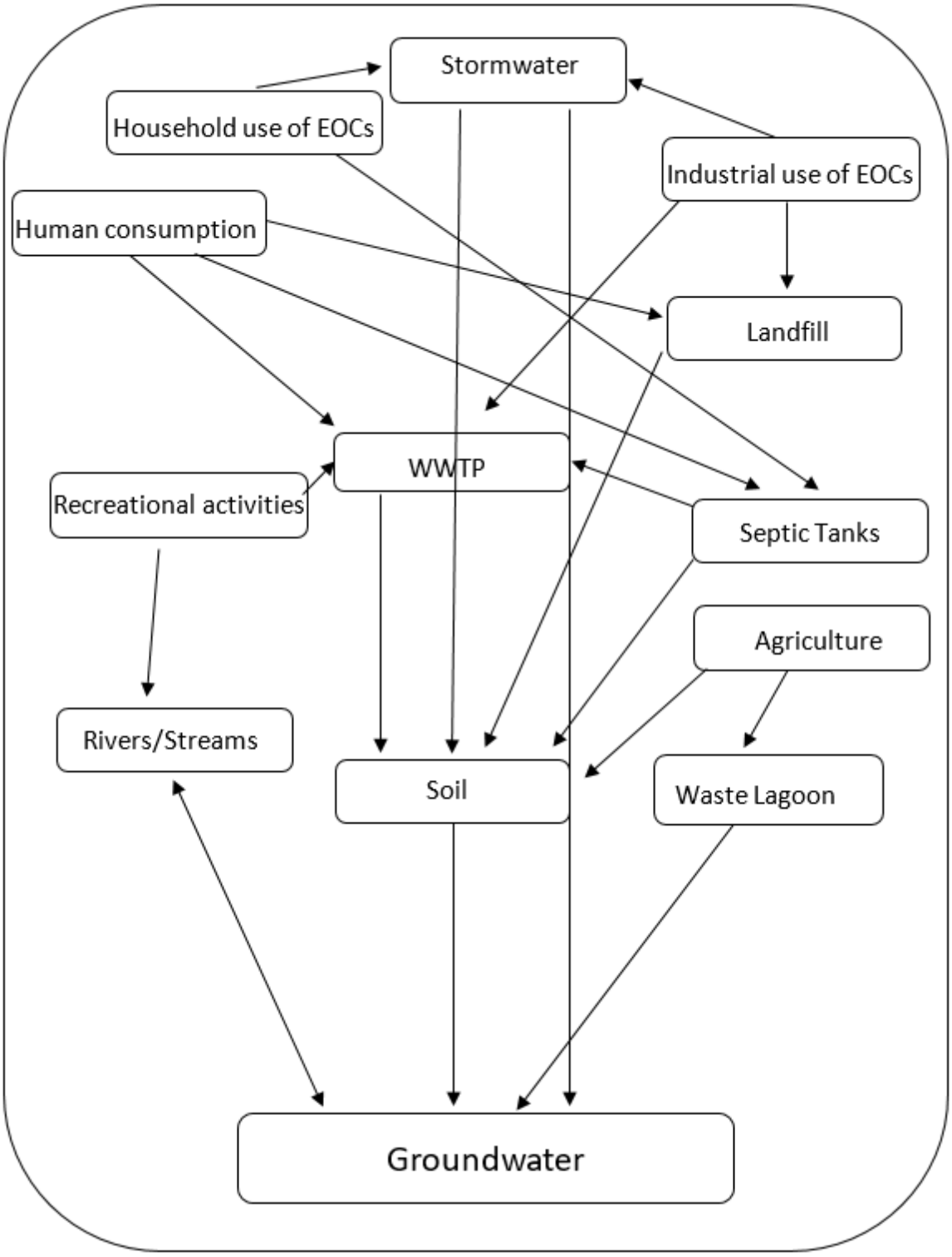


Figure 1.2: Sources of EOC contamination to groundwater

1.3.2 Reported Concentrations of EOCs in Groundwater

To date most overseas studies on EOCs have focused on wastewater and surface water compared to groundwater [19]. This may in part be because wastewater is the main source of EOCs to the environment. Waste water and surface water are often thought to be more contaminated compared to groundwater which receives protection from the surface above. Groundwater is also more difficult to gain access to and the sampling protocol is more difficult and time consuming. The target analytes of this study along with the concentration range detected in groundwater in overseas countries are presented in Table 1.1. Data was not available for all target analytes.

Table 1.1: Internationally reported concentrations of target analytes in groundwater

Compound	Use	Range (ngL^{-1})	Reference
Estrone (E1)	Natural hormone	1.6-390	[41] [42] [43]
17β-estradiol (E2)	Natural hormone	0.79-4.7	[41] [42]
Estriol (E3)	Natural hormone	0.16	[42]
17α-ethinyl-estradiol (EE2)	Synthetic hormone	0.94	[42]
17α-estradiol	Metabolite of 17β-estradiol	3.41-5.17	[41]
Testosterone	Natural hormone	30	[43]
Androstenedione	Natural hormone	0.8	[44]
Bisphenol A (BPA)	Industrial chemical	930	[42]
3-phenoxybenzoic acid (3 PBOH)	Metabolite of insecticide	*	
Chloroxylenol	Antiseptic/disinfectant	*	

***o*-phenylphenol (OPP)**	Antimicrobial	*	
4-tert-Octylphenol (OP)	Industrial Chemical	42-190	[42, 45]
Chlorophene	Preservative	*	
Nonylphenol (NP)	Industrial Chemical	1500	[42]
Benzophenone-1 (BP-1)	UV-filter	19.4	[46]
Benzophenone-3 (BP-3)	UV-filter	4.36-34	[47]
4 - methylbenzylidene camphor (4-MBC)	UV-filter	13.9-3625	[46] [48-49]
2-ethylhexyl-p-methoxycinnamate (OMC)	UV-filter	*	
Methyl paraben (mParaben)	Preservative	36-459	[48-49]
Ethyl paraben (eParaben)	Preservative	64-86	[49]
Propyl paraben (pParaben)	Preservative	3-61.9	[48-49]
Butyl paraben (bParaben)	Preservative	19-32	[49]
Benzyl paraben	Preservative	*	
Triclosan	Antimicrobial	8.7-39.9	[50]
Methyl Triclosan	Antimicrobial	*	

* = No literature available

1.3.3 Target Analytes

The target analytes for this research were chosen based on their frequency and concentrations reported in the literature. A suite of Emerging Organic Contaminants was chosen including steroid hormones, uv-filters, preservatives and industrial compounds. Their use and occurrence and behaviour in the environment is outlined in Table 1.2 which also lists their chemical structures and key physical characteristics.

Industrial Compounds

Industrial compounds are used in cleaning products, degreasers and detergents and include compounds such as, octylphenol (OP) and nonylphenol (NP). These industrial compounds have been identified as endocrine disruptors [51]. NP is widely used as a surfactant; due to its high hydrophobicity and low solubility. Due to NP physicochemical properties it accumulates in parts of the environment with high organic content e.g. Sewage sludge. Nonylphenol has been classified by the World Health Organization (WHO) as an endocrine disruptor, and has shown to exert estrogenic responses on aquatic organisms [52]. NP acts as an endocrine disruptor by mimicking the natural hormone 17β estradiol and competing for the binding site of the natural oestrogen[52]. Both OP and NP have been previously detected in rural groundwater due to agricultural activities [53]. NP has been detected at concentrations up to 55.3 μg/L in drinking water [52]. In 2008 the European Water Framework Directive 2015 placed nonylphenols on a list of priority hazardous substances for which environmental quality standards were set, drinking water values of 0.3 μg /L and 2 μg/L for surface waters were set [52].

Bisphenol A (BPA) a classified endocrine disruptor [54] may also be considered an industrial compound as it is used as a raw material in the production of polycarbonate plastics and epoxy resins. Over 3 million tons per year of BPA is used worldwide for the manufacture of numerous products [55], such as food can lining [56], receipt paper and reusable water bottles [57], drinking water pipe linings and electrical equipment [54]. Bisphenol A has shown numerous negative effects on animals at a low dose including reproductive effects [58], early onset of puberty [59], decreased maternal behaviours [60] and increased rate of cancers [61]. Bisphenol A is detected at trace levels in

the receiving environment including river water, coastal waters [62], air [63], and groundwater due to anthropogenic activities, landfill disposal, effluent from wastewater treatment plants and indirect release during manufacture [54].

Organic UV Filters

Sun protection cosmetics have been used for almost 85 years [64]. They work by containing uv-filters which absorb UV radiation and thus protecting the skin. UV-filters are compounds which normally possess conjugated carbon-carbon bonds and/or carbonyl groups or aromatic structures, this enables them to attenuate the transmission of solar photons that reach the Earth's surface [64]. UV-filters are not only used in personal care products, they are also used in plastic to prevent light induced degradation. UV-filters enter the environment through bathing, washing clothes, WWTPs, and through swimming and sunbathing [65 66].

Two of the target analytes from this study, 4-MBC and OMC have shown to exhibit estrogenic activity in the human breast cancer cell (MCF-7). Animal studies have shown that UV-filters can disrupt thyroid activity, OMC was shown to cause a dose dependent decrease in TSH, T4 and T3 serum in rats [67]. Parent rats treated with 4-MBC gave birth to offspring with increased thyroid weight and T3 concentrations [68]. Puberty in male rats was delayed when treated with 4-MBC however no effects on females were observed [68]. Another concern regarding organic uv-filters is their ability to bioaccumulate in the environment due to their high lipophilicity and high stability [65]. Two uv-filters, BP-3 and OMC have been shown to bioaccumulate in fish at up to mid ng/g levels [65], similar to levels of PCBs and DDT [69].

Preservatives

Parabens are a class of preservatives commonly found in pharmaceutical, personal care and food products [70]. Parabens in food and beverages are much less common however, and can be recognized on an ingredients list as additives E214-219. Although parabens can be readily degraded under aerobic conditions, they are still a concern and are considered 'pseudo persistent' due to their high use and release into the environment [70]. In some *in vitro* screening tests parabens have shown to exhibit estrogenic activity, including ligand binding to the estrogen

receptor, regulation of CAT gene expression, and proliferation of MCF-7 human breast cancer cells [71]. *In vivo* studies have reported increased uterine weight (ethyl-, propyl-, butyl-, isobutyl, and benzyl-paraben in young female rodents. *In vivo* studies in males (butyl-, propyl- paraben) has shown to cause reproductive tract effects [72]. Bacteria in WTTPs have shown resistance to parabens, it is hypothesized that paraben resistance develops due to the continuous exposure of parabens [73]. Parabens have shown to inhibit algal growth at concentrations of 5000 μgL^{-1} however, this is not observed at environmentally relevant concentrations of 0.5 μgL^{-1} [74].

The European Union sets maximum concentrations of 0.4% (w/w) for each paraben for the use in cosmetics, [70] and the European food safety authority has set an acceptable daily intake (ADI) of a total of 0-10 mg/kg bodyweight per day for methyl and ethyl paraben [75].

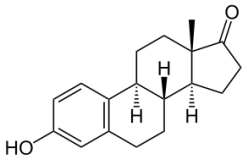
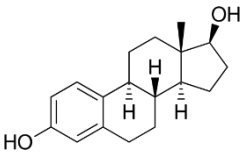
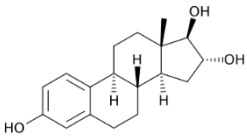
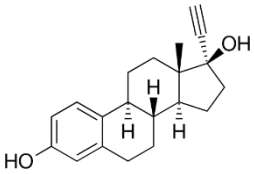
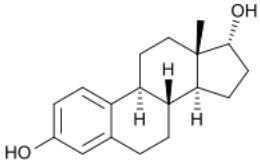
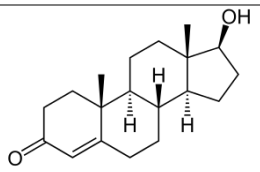
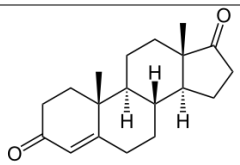
Steroid Hormones

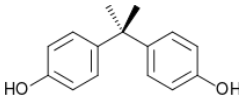
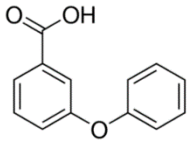
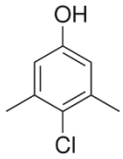
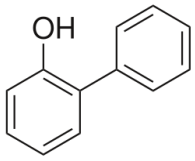
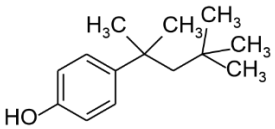
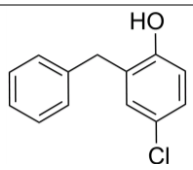
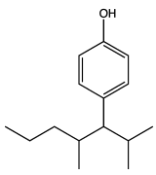
Steroid hormones are excreted by humans and animals into the environment. Some of these hormones are naturally produced by mammals whereas others are synthetic compounds ingested by humans as medication e.g. the contraceptive pill, containing the active ingredient 17α-ethinyl-estradiol (EE2). Hormones have been reported in groundwater in Austria [42], Germany [10], France [44], China [76] and the UK [20]. Hormone concentrations in groundwater are usually in the low ng/L range. This is because hormones are likely to sorb onto soil particles due to their low aqueous solubility and moderate hydrophobicity [77]. They may also biodegrade [78]. Low environmental concentrations however should not be disregarded as estrogenic effects have been observed at concentrations of as low as 1 ng/L for 17β-estradiol and 17α-Ethinyl estradiol [51]. Concentrated animal feeding operations and land irrigation with reclaimed water are likely to increase hormone concentrations in groundwater [43]. Animal manure is also a major source of natural steroids to the environment [44]. Steroid hormone excretions per year for farm animals in Europe is estimated at 33 tons' of estrogens, 7.1 tons' androgens and 322 tons' progestogens [79].

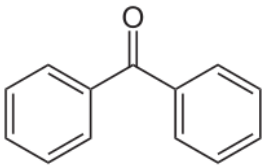
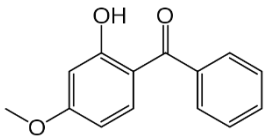
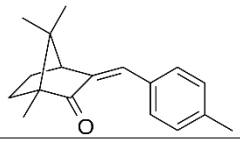
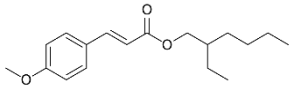
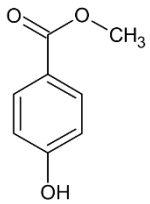
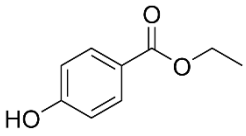
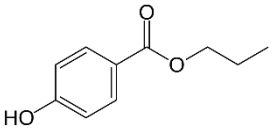
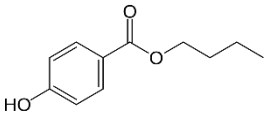
Triclosan

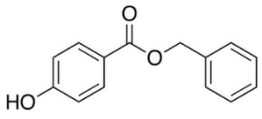
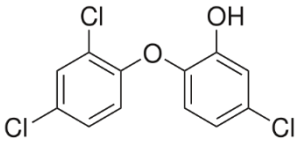
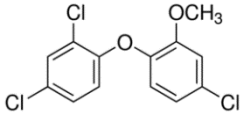
Triclosan is an antimicrobial agent present in household and personal care products such as toothpaste, hand soaps and deodorants[80]. Triclosan enters aquatic systems such as surface waters and waste water during consumer and industrial use[80]. Triclosan shows incomplete removal during wastewater treatment [81] and has been detected throughout the environment including surface waters, soil and human breast milk [82]. Research regarding the effect of triclosan on human health is ongoing, many studies have already described its toxic effects on animals [83] and freshwater organisms [84] including premature metamorphosis in tadpoles [84], decreased sperm production in rats [85] and depression of the central nervous system in mice [86]. When released into the environment triclosan has shown toxicity towards algae [87], exhibiting effects on its growth at concentrations below 1 μgL^{-1} [88]. This is critical as algae are first step producers in the food chain therefore this could have a detrimental effect on an ecosystem [89].

Table 1.2: List of emerging contaminants selected as analytes for this research including key physical parameters and use (obtained from Chemspider database)

Name	Structure	CAS	LogD at pH 7.4 [a]	Log Koc [b]	BCF at pH 7.4 [c]	Use
Estrone (E1)		53-16-7	3.62	3.35	334	Natural hormone
17β-estradiol (E2)		50-28-2	4.15	3.36	832	Natural hormone
Estriol (E3)		50-27-1	2.53	2.75	49	Natural hormone
17α-ethinyl-estradiol (EE2)		57-63-6	4.11	3.61	776	Birth control pill
17α-estradiol		57-91-0	3.62	3.34	329.27	Natural hormone released by farm animals
Testosterone		58-22-0	3.16	3.09	147.62	Natural hormone
Androstenedione		63-05-8	2.90	2.95	94.68	Natural hormone

Name	Structure	CAS	LogD at pH 7.4 [a]	Log Koc [b]	BCF at pH 7.4 [c]	Use
Bisphenol A (BPA)		80-05-7	3.63	3.35	336.40	Industrial chemical
3-phenoxybenzoic acid (3 PBOH)		3739-38-6	0.91	3.30	1.00	Metabolite of insecticide
Chloroxylenol		88-04-0	3.30	3.17	190.43	Antiseptic and disinfectant
***o*-phenylphenol (OPP)**		90-43-7	3.08	3.05	129.34	A biocide used as a preservative
4-tert-Octylphenol (OP)		140-66-9	4.68	3.92	2125.39	Industrial chemical
Chlorophene		120-32-1	4.31	3.72	1116.02	Preservative
Nonylphenol (NP)		25154-52-3	6.13	4.70	26602.85	Detergent and used in industrial manufacturing

Name	Structure	CAS	LogD at pH 7.4 [a]	Log Koc [b]	BCF at pH 7.4 [c]	Use
Benzophenone-1 (BP-1)		119-61-9	2.96	2.98	104.35	UV blocker
Benzophenone-3 (BP-3)		131-57-7	3.65	3.25	309.75	UV light absorber
4 -methylbenzylidene camphor (4-MBC)		36861-47-9	4.76	3.96	245639	UV blocker
2-ethylhexyl-p-methoxycinnamate (OMC)		5466-77-3	5.19	4.20	5205.12	UV light absorber
Methyl paraben (mParaben)		99-76-3	2.09	2.49	22.35	Anti-fungal agent
Ethyl paraben (eParaben)		120-47-8	2.48	2.70	43.85	Anti-fungal preservative
Propyl paraben (pParaben)		94-13-3	2.81	2.88	78.29	Anti-fungal preservative
Butyl paraben (bParaben)		94-26-8	3.12	3.04	134.12	Anti-microbial preservative

Name	Structure	CAS	LogD at pH 7.4 [a]	Log Koc [b]	BCF at pH 7.4 [c]	Use
Benzyl paraben (bzParaben)		202-311	3.44	3.21	233.76	Anti-microbial agent
Triclosan		3380-34-5	5.13	4.09	4269.68	Antibacterial and anti-fungal
Methyl Triclosan		4640-01-1	5.52	4.37	9160.68	Degradation product of triclosan

[a] pH 7.4 adjusted K_{OW}, i.e. Distribution coefficient of ionized plus un-ionized compound between n-octanol and water (K_{OW} also referred to as logP).

[b] Distribution coefficient of compound between the soil organic carbon and water phase.

[c] Estimated bioconcentration factor at pH 7.4

1.3.4 Human Health and Ecological Effects of Emerging Organic Contaminants

Most EOCs are typically present in aquatic ecosystems at parts per trillion to parts per billion concentrations [90]. Despite these low concentrations, ecological exposure has resulted in endocrine disruption [91] effects on growth and reproduction [92], genotoxicity [93], organ damage [94], and changes in behaviour [95]. Examples include, reproductive issues in fish e.g. intersex fish (where fish have both male and female sex organs) [96], lowered hormone levels [97] and reduced fertilization capability and gamete production [98]. A decline in certain species such as the American alligator due to increased sterility [99] and eggshell thinning in birds and reptiles is also thought to be caused by EOCs in the environment.

Observations in the environment have raised concern over potential human health effects due to hormone receptor systems functioning similarly in humans and animals. However, data regarding human health is limited. Recent studies have linked exposure to EOCs to reproductive disorders [100] and thyroid functioning in humans [101]. Key studies have presented increased occurrences of malformed reproductive organs in new born boys, early onset of puberty in girls [102], along with an increase in endocrine-related human diseases including endometriosis [103].

Laboratory studies have shown adverse developmental exposure in both males and females [104]. In males, EOCs have been associated with testicular germ cell cancer [105], urogenital tract malformation [106] and decreased sperm count [107]. Similarly, in females EOCs are associated with numerous reproductive disorders and breast cancer [108]. Recent studies have shown EOCs can impact the development of diabetes, obesity [109] and cardiovascular disease [110].

1.4 Environmental Fate of Emerging Organic Contaminants

Emerging organic contaminants comprise a wide range of compounds with diverse structures and physicochemical properties. The physicochemical properties of a compound can be used to predict its environmental fate [19]. These properties include, pK_a (dissociation constant), pK_{ow} (octanol water partitioning coefficient), $logK_{oc}$ (sorption coefficient), $logK_d$ (water distribution coefficient), solubility, hydrophilicity and hydrophobicity (Table 1.3). Hydrophilic EOCs are water soluble and travel more easily in the environment, whereas hydrophobic EOCs are associated with the solid phase (sediment) thus usually more persistent [24]. Environmental factors can also influence a compounds fate in the environment [19]. These factors include, groundwater residence time, redox conditions, total loading, soil type, total suspended sediment, chemical oxygen demand, biological oxygen demand, pH, and nutrient availability.

Depending on the physicochemical properties and environmental factors, EOCs can be either attenuated by sorption to surfaces, degraded by biodegradation or photolysis, or migrate through the unsaturated and saturated zone to groundwater [111]. To date there is insufficient information on EOCs fate in the environment and the data that is available is only from a small number of studies.

Table 1.3: Physicochemical properties important for predicting the fate of EOCs in the environment and their definitions

Physicochemical Property	Definition
pK_a (acid dissociation constant)	A measure of the strength of an acid in solution
pK_{ow} (octanol water partitioning coefficient)	The ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase
$logK_{oc}$ (sorption coefficient)	A measure of the mobility of a substance in soil
$logK_d$ (water distribution coefficient)	A measure of sorption and is defined as the ratio of the quantity absorbed and the quantity in solution
solubility	Solubility is the property of a chemical substance to dissolve in solid, liquid or gaseous solvent.
hydrophilicity	Having an affinity for water, readily absorbing or dissolving in water
hydrophobicity	Having no affinity for water, incapable of dissolving in water

Groundwater Ubiquity Score (GUS)

The physical and chemical properties of a compound can influence its potential for leaching through soil to groundwater. These factors include, sorption (Log K_{oc}) and its persistence in soil ($T\frac{1}{2}$). The groundwater ubiquity score or GUS was originally proposed by Gustafson in 1989 to predict the potential for pesticides to move towards groundwater [112]. The GUS score can be calculated from the half-life of soil ($T\frac{1}{2}$, days), and the K_{oc} (ml/g). Although the GUS score was originally designed for the assessment of pesticides it can also be applied to other compounds. A study by [113] X Jian et al (2009) used GUS to predict the leachability of nine EOCs including OP, BPA, NP and triclosan, the study concluded that the GUS model was accurate in predicting leaching potentials of the compounds, however was unable to provide quantitative results. The chemical properties used to derive GUS's for the target analytes of this study are listed in Table 1.4. A GUS score below 0 equates to an extremely low level of leaching potential, applicable for 9/25 of the target analytes within this study. A GUS between 0-1.8 is representative of low leaching potential, 9/25 of the target analytes fall within this range and a GUS between 1.8-2.8 is characteristic of a moderate leaching potential, this is applicable for 6/25 target analytes. Only one of the compounds, methyl paraben had a high leaching potential, characterised by a GUS value above 2.8.

Equation 1: Groundwater ubiquity score

$$GUS = logT\frac{1}{2} \times (4 - log\ K_{oc})$$

Table 1.4: Groundwater ubiquity scores of target analytes

Contaminant	Log K_{oc}	$T\frac{1}{2}$ soil	MW (Da)	S (mg L^{-1})	GUS	Leaching
estrone	4.375	75	270.37	146.8	-0.703148	E. low
17β-estradiol	4.186	75	272.39	81.97	-0.348761	E. low
Estriol	3.082	75	288.39	440.8	1.721306	Low
17α-ethinyl	4.65	120	296.41	116.4	-1.351468	E. low
17α-estradiol	3.3435	75	272.382	81.97	1.2309777	Low
Testosterone	3.339	75	288.43	67.76	1.239415	Low
Androstenedione	2.95622	120	286.409	65.97	2.1702078	Moderate
BPA	4.576	75	228.29	172.7	-1.080035	E. low
3PBOH	2.352	30	214.217	16.91	2.4342958	Moderate
Chloroxylenol	2.906	75	156.61	434.6	2.051317	Moderate
OPP	3.828	30	170.21	535.8	0.254065	Low
OP	3.999	75	206.33	4.821	0.001875	Low
Chlorophene	4.285	75	218.68	112	-0.534392	E. low
NP	4.583	30	220.36	1.57	-0.861162	E. low
BP-1	3.056	30	182.218	103.3	1.394402	Low
BP-3	2.98	75	228.25	68.56	1.912562	Moderate
4-MBC	4.089	120	254.38	0.1966	-0.185047	E. low
OMC	3.935	30	290.41	0.1548	0.096013	Low
Methyl paraben	1.936	30	152.15	5981	3.048778	High
Ethyl paraben	2.197	30	166.18	1894	2.66325	Moderate
Propyl paraben	2.457	30	180.21	529.3	2.279198	Moderate
Butyl paraben	2.718	17.3	194.23	159	1.587175	Low
Benzyl paraben	3.703	30	228.243	107.8	0.438705	Low
Triclosan	4.369	75	289.55	4.621	-0.691898	E. Low
Methyl triclosan	5.22	120	303.568	0.4044	-2.536601	E. Low

1.5 Thesis Rationale and Objectives

Emerging organic contaminants have been detected in groundwater internationally. While previous work in New Zealand has investigated EOCs in surface water [114], sediment and effluent [115], there are no existing studies in New Zealand focusing on groundwater.

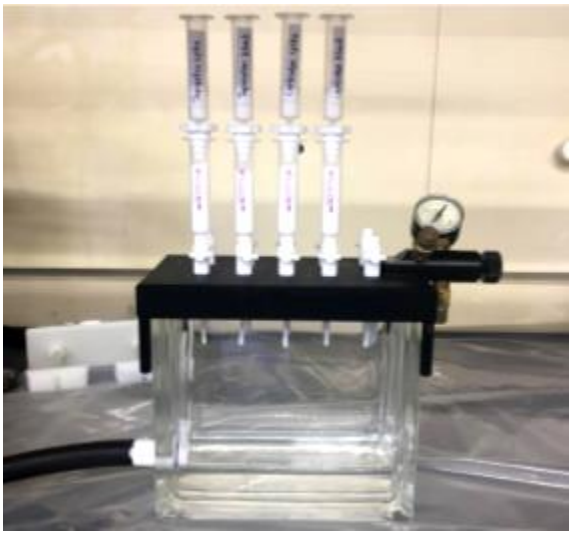
The overall aim of this thesis was to determine the types and concentrations of emerging contaminants in Canterbury soil, effluent and groundwater.

The specific objectives were to:

1. Develop and validate a novel method for the extraction and clean-up of EOCs from soil and particulate samples
2. Determine the concentrations of EOCs in soil and effluent.
3. Sample shallow groundwater wells (<25m depth) from across the Canterbury region for a suite of EOCs.
4. Undertake a risk assessment based upon the current concentrations of EOCs detected in Canterbury groundwater.

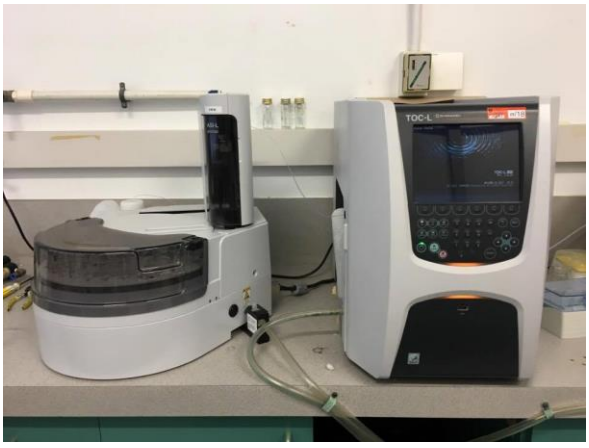
1.5.1 Thesis Layout

Chapter 1 introduces the reader to the target emerging contaminants for this study and the importance of groundwater. The methods are outlined in Chapter 2 used for sample preparation, sample extraction and sample analysis. Chapter 3 introduces potential sources of EOCs to groundwater along with development and validation of a novel method for the extraction and clean-up of soil and effluent samples. The developed method is then applied to the collected soil, particulate and effluent samples. In Chapter 4 the results from the sampling and analysis of groundwater across the Canterbury region carried out across two seasons are presented. In Chapter 5 the results from Chapter 4 are used to determine the risk current levels EOCs pose to aquatic life and human health. Chapter 6 draws together the conclusions from the findings in Chapters 3 - 5 and discusses the implications and potential future work arising from this research.



CHAPTER TWO

METHODS



2 Methods

2.1 Introduction

This chapter outlines the experimental methods used in this thesis. Solid phase extraction was used for all groundwater and effluent samples excluding one effluent sample (DS1) which was freeze dried and extracted following the method used for soil. An ultrasonic extraction method was used to extract the soil and sediment samples followed by enhanced matrix removal (EMR) clean-up, this method will be described in this chapter with the method development presented in Chapter Three. All samples collected were analysed at the University of Canterbury using the GC-MS method validated in-house by Gemma Wadworth [114]. The sampling protocols are described in the relevant chapters.

2.1.1 Chemicals

Standards of mParaben, eParaben, pParaben, bParaben, 4-MBC, BP-3 and OMC were purchased from Accustandard (New Haven, CT.) Standards of chloroxylenol, chlorophene, BP-1, 3-PBOH, BPA, NP, estrone (E1), 17β estradiol (E2), estriol (E3), 17α ethinylestradiol (EE2) were purchased from Sigma Aldrich (St. Louis, MO). Standards of triclosan and methyltriclosan were purchased from Dr. Ehrenstorfer Gmbtl (Augsburg, Germany) and OP was purchased from Supelo Analytical (Bellefonte, PA). Standards of 17α estradiol, androstenedione, testosterone and estriol were purchased from Sigma Aldrich NZ Ltd. Standard solutions were combined and diluted to produce a 1 μg mL^{-1} native mix in ACN.

The internal standard BPC was purchased from Sigma Aldrich (St. Louis, Mo) Further internal standards included $^{13}C_2$mEHP, $^{13}C_2$mEP, $^{13}C_6$3phenoxybenzoic acid purchased from Cambridge Isotope Laboratories Inc. (Cambridge, UK) and Estrone-d4, 17β estradiol-d4, 17α ethinylestradiol-d4 were purchased from CDN Isotopes, Quebec, Canada. An internal standard stock mix was made by combining the standards to form a 1 μg mL^{-1} internal standard mix in ACN.

Carbon-13 labelled surrogates including, $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, $^{13}C_6$-E2 were purchased from Cambridge Isotope Laboratories Inc. (Cambridge, UK.)

The surrogates were combined to make a 1 µg mL^{-1} master mix in ACN which was added to each sample.

All solvents used in this study were HPLC grade and were purchased from Fisher Scientific (Fair Lawn, New Jersey) including methanol (MeOH), acetone, dichloromethane (DCM), acetonitrile (ACN), toluene and isooctane. Ultrapure (18MΩ cm^{-1}) water was sourced from an onsite water purification system (Sartorius Stedim, Arium® pro UV, Biotech). Sulphuric acid (conc. ACS reagent) and phosphoric acid was purchased from Mallinckrodt Baker Inc (Phillipsburg, NJ). Sodium sulfate anhydrous, granulated was purchased from Sigma Aldrich. Decon90 (5L) was purchased from Decon Laboratories Ltd (Sussex, UK).

N-Methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) was purchased from Sigma Aldrich. Helium gas was purchased from BOC gases.

Solid potassium hydrogen phthalate, solid sodium hydrogen carbonate, solid sodium carbonate, solid sucrose, solid sodium bicarbonate was purchased from Sigma Aldrich.

2.1.2 Materials

Solid phase extraction cartridges (strataX, 1g/20mL) and Florisil clean-up cartridges (1g/6mL, mesh <250 µm) were purchased from IST Isolute and GF/C (47mm) filter papers were purchased from Whatman.

Bond Elut EMR – Lipid dSPE 1 g in 15 mL tube (p/n 5982-1010) and Bond Elute final polish for Enhanced Matrix Removal 2 g in 15 mL tube (p/n 5982-0101) were purchased from Agilent, Ottawa sand was purchased from Restek.

The GC-MS syringe (10 µL) was purchased from SGE Analytical Science. The glass liners (splitless, single taper gooseneck with wool, 3.5mm x 5.0 x 95) and septa (BTO Shimadzu Plug) were purchased from Restek.

2.2 Solid Phase Extraction (SPE)

2.2.1 Sample Extraction

On immediate return to the laboratory samples were acidified with concentrated sulphuric acid to a pH of 2. Prior to solid phase extraction 4L groundwater and 1L effluent samples were vacuum filtered through 1.2 μm pore GF/C filters (Whatman) (Figure 2.1). Filter papers were extracted and analysed separately. Following filtration all samples were spiked with 50 μL of the 1μg mL^{-1} 13C surrogate solution. Spiked samples were spiked with 50 μL of the 1μg mL^{-1} native mix. Comparative standards were dispensed at the same time as spiked samples. Groundwater and effluent samples were extracted within 48 hours of sampling as recommended by the U.S Environmental Protection Agency [116] .

Strata-X cartridges were pre-conditioned with 3 x 5 mL aliquots of Acetone followed by 3 x 5 mL Methanol and 3 x 5 mL MQ water. Pre-conditioning was carried out by positioning the SPE cartridges on the manifold whilst the taps were closed to prevent flow. A 5-mL aliquot of the designated solvent was added to each cartridge, the taps were opened and approximately half the solvent allowed to flow through under gravity. The taps were then closed for 2 minutes, during this time the solvent could saturate the SPE bed. After this time, the taps were opened allowing the solvent to pass through. This process was repeated nine times, three times with each solvent. The last conditioning was three individual aliquots of ultrapure water, this step ensured the removal of previous solvents without exposing the SPE bed to air.

Solid phase extraction took place on a VacMaster Sample Processing Station (Biotage). The sample bottles were connected to Teflon end caps which plugged into the SPE cartridges by Teflon transfer tubes. The taps on the SPE manifold were opened allowing a flow rate of approximately 20 mL min^{-1} under a slight vacuum (Figure 2.2). The flow was stopped by turning the tap to the off position once the sample had passed through the SPE cartridge and the bottle and SPE tubing rinsed by passing through 20 ml ultrapure water.

Finally, the cartridges were completely dried under vacuum for ~ 3-4 hours. The elution of target compounds was carried out by stacking the Strata-X cartridges (previously used for extraction)

above Strata FLPR (Florisil pesticide grade) cartridges 3/4 filled with pre-baked sodium sulfate anhydrous and pre-rinsed with 3 x 5 mL aliquots of acetone (Figure 2.3). Cartridges were eluted with 6 x 5 mL of Acetone into solvent rinsed 30 mL amber glass vials. Each 5-mL aliquot of acetone was allowed to sit on the SPE bed for 2 minutes before being allowed to pass through under gravity. Vials were capped and stored at 4°C until sample concentration.

2.2.2 QA/QC

All equipment and glassware was solvent rinsed following the method outlined in section 2.9. The sodium sulfate used for drying was rinsed with MeOH and ACN in a schott bottle and then baked overnight at 500°C. The GF/C filter papers were also pre-cleaned with MeOH and ACN and dried under vacuum prior to their use. Sodium sulfate was added to the bottom of the acetone bottle to remove residual water.

In each sample batch, a field blank, duplicate sample, spike sample, cartridge blank and cartridge spike was included and were extracted at the same time as the samples. All samples, field blanks cartridge blanks and cartridge spikes were spiked with 50 µL of the 1 µg mL^{-1} 13C surrogate mix to calculate analyte recovery of the SPE method. Prior to solid phase extraction, comparative standards were dispensed at the time of spiking containing 50 µL of the 1 µg mL^{-1} 13C surrogate mix and 50 µL of the 1 µg mL^{-1} native mix. Spike recoveries were calculated based on the concentration in the sample spike out of the concentration in the comparative. Any analytes detected in the cartridge blank or field blanks were used to correct for analytes reported in the results.

2.2.3 Method Performance

Due to the method already being prior validated [114], method performance was checked by ensuring recovery of analytes and surrogates were within an acceptable range. The recoveries of most analytes were within an acceptable range (Defined as ~70% - 120%) [117] (Table 2.1 and

Table 2.3). Analytes which were greatly outside the acceptable range included, chloroxylenol, OPP, E1 and androstenedione, with recoveries of 262%, 343%, 642% and 46% respectively. The

reason for extremely high recoveries is thought to be a derivatization issue. Due to these analytes having unacceptable recoveries they have been excluded from the results.

2.2.4 Limits of Detection

The limits of detection were determined using EPA Method 8280A. The limits of detection are provided in Table 2.2 and Table 2.4.

Figure 2.1 Vacuum filtration set-up for groundwater and effluent samples

Figure 2.2. Solid phase extraction of 4L groundwater samples

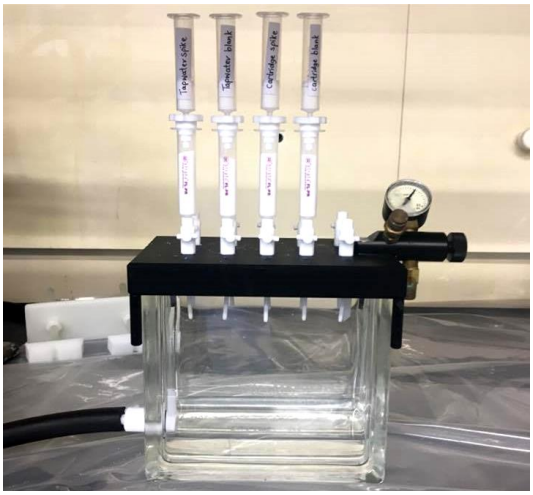


Figure 2.3: Elution of extracts, strataX cartridges stacked above Florisil cartridges.

Table 2.1: Spike recoveries of target analytes from 4L groundwater.

Analyte	Average % Recovery 4L groundwater (n=9)	Std Dev	95% C.I.
Androstenedione	45.5	38.4	25.1
BPA	99.5	44.0	28.7
bParaben	104.1	19.8	12.9
BP-1	84.1	38.3	25.0
BP3	116.8	52.1	34.0
bzParaben	116.0	23.5	15.3
chlorophene	109.3	19.6	12.8
chloroxylenol	261.5	178.1	116.4
eParaben	155.2	51.8	33.8
E1	641.6	603.5	394.3
E2	97.5	13.5	8.8
EE2	90.1	10.2	6.7
E3	99.5	35.0	22.9
17α Estradiol	106.0	15.0	9.8
4MBC	115.7	30.1	19.7
mparaben	191.4	87.1	56.9
mTric	87.6	17.6	11.5
NP	76.2	12.3	8.0
OMC	64.7	11.2	7.3
OP	116.9	51.0	33.3
OPP	343.2	256.9	167.9
3PBOH	112.4	31.9	20.9
pParaben	101.4	26.0	17.0
Testosterone	90.8	30.3	19.8
Testosterone	90.8	30.3	19.8
Tric	102.8	21.1	13.8

Table 2.2: Limits of detection of analytes in groundwater, with lower and upper limits at 95% confidence.

Analyte	Limits of Detection (Groundwater, ng L^{-1})	Lower limit	Upper limit
Androstenedione	0.324	0.245	0.402
BPA	0.026	0.012	0.040
bParaben	0.097	0.054	0.140
BP-1	0.042	0.000	0.096
BP3	0.086	0.005	0.167
bzParaben	0.182	0.097	0.266
chlorophene	0.117	0.072	0.162
Chloroxylenol	0.026	0.020	0.032
eParaben	0.042	0.019	0.065
E1	3.870	3.379	4.361
E2	0.155	0.108	0.201
EE2	0.212	0.000	0.484
E3	0.319	0.000	0.817
17α Estradiol	0.430	0.000	1.005
4MBC	0.176	0.113	0.239
mparaben	0.021	0.006	0.037
mTric	0.486	0.212	0.760
NP	0.056	0.051	0.061
OMC	0.205	0.139	0.271
OP	1.140	0.020	2.259
OPP	0.042	0.018	0.066
3PBOH	0.220	0.189	0.251
pParaben	0.137	0.090	0.185
Testosterone	0.034	0.015	0.052
Tric	0.088	0.057	0.119

Table 2.3: Spike recoveries and statistical summary of 13C labelled surrogates from 4L groundwater

Isotope Surrogates	Average % Recovery 4L groundwater (n=9)	Std Dev	95% C.I.
BPA (ring 13C12)	89.2	15.5	10.1
bParaben (ring 13C6)	105.3	24.1	15.7
E2 (ring 13C6)	102.3	11.0	7.2
mParaben (ring 13C6)	160.7	73.4	47.9
NP (ring 13C6)	101.3	22.8	14.9
Tric (ring 13C12)	94.5	17.9	11.7

Table 2.4: Limits of detection of 13C surrogates in groundwater, with lower and upper limits at 95% confidence

Analyte	Limits of Detection (Groundwater, ng L^{-1})	Lower limit	Upper limit
BPA (ring 13C12)	0.014	0.008	0.021
bParaben (ring 13C6)	0.044	0.033	0.056
E2 (ring 13C6)	1.624	0.636	2.613
mParaben (ring 13C6)	0.040	0.023	0.058
NP (ring 13C6)	0.110	0.105	0.115
Tric (ring 13C12)	0.230	0.143	0.317

2.3 Extraction of Soil and Particulates

A novel method was developed in house for the extraction of the target analytes from soil and particulates. Full method development is detailed in Chapter Three. This method utilised a new 'dispersive solid phase extraction kit' from Agilent specifically designed to remove lipids from high fat samples, but usable for any sample type. The kit contained 1 g of preweighted proprietary sorbent in 15 mL centrifuge tubes, the sorbent removes interfering lipids from the sample whilst leaving the analytes of interest behind. The final polishing step containing $MgSO_4$ removes excess water and improves analyte partitioning. Enhanced matrix removal (EMR) clean-up was optimized by varying the amount of ultrapure water added for activation.

2.3.1 Sample Preparation

Soil samples were stored at -15°C to prevent bacterial breakdown of target analytes. The moisture content of soil was calculated by drying a subsample in a drying oven at 105°C for 24 hours. Particulate samples were collected from the filtration of groundwater and effluent samples, filter papers were wrapped in aluminium foil which had been precleaned with MeOH and stored at -15°C.

2.3.2 Sample Extraction of Soil and Particulates

Particulate samples were transferred and 5 g soil samples were weighed into 50 ml glass centrifuge tubes. Respective samples were spiked with 50 μL of the 1 ppm native mix and 50 μL of the 1ppm 13C surrogate mix was added to every sample. At this time a comparative sample was dispensed containing 50 μL of the 1 ppm native mix and 50 μL of the 1ppm 13C surrogate mix. Acetonitrile (10 mL) was added to each centrifuge tube, and the samples were extracted for 10 minutes using the sweep function on an ultrasonic bath. Subsequently, samples were centrifuged at 2500 rpm for 5 minutes. The extract was decanted to solvent rinsed 30 mL amber vials, and the extraction process was repeated twice more. Prior to centrifugation it was important to degas the centrifuge tubes by opening the sample momentarily to the atmosphere then replacing the lid. This was due to gas build up during ultrasonication. Following extraction,

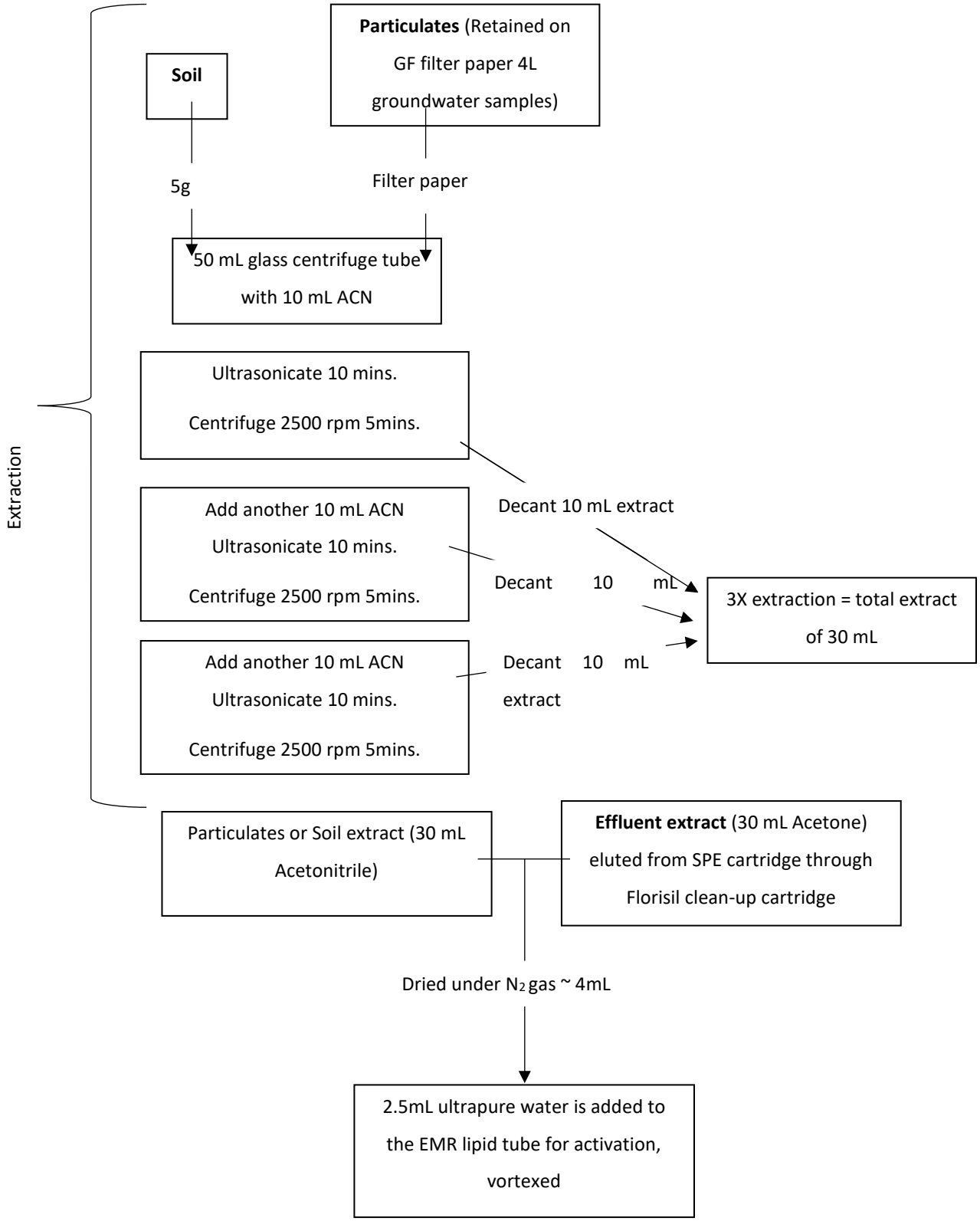
the solvent was evaporated under a gentle N_2 stream until approximately 4 mL remained. Extracts were then ready for the clean-up process. For activation, 2.5 mL of ultrapure water was added to the EMR lipid tube and vortexed. The 4-mL extract was quantitively transferred to the ERM tube to give a total ACN volume of ~5 mL. The tube was vortexed, centrifuged for 5 minutes at 4500 rpm, and the upper ACN layer was transferred to the polish tube. It was important that once the extract was added to the polish tube, it was vortexed immediately and for a further 1 minute to avoid clumping. Following this the polish tubes were centrifuged at 4500 rpm for 1 minute and the extract decanted to solvent cleaned 15 mL amber glass vials. The vials were capped and stored at 4°C until sample concentration. After extraction and clean-up, the analytes were detected and quantified using gas chromatography mass spectrometry. ^{13}C labelled compounds ($^{13}C_6$mParaben, $^{13}C_6$bParaben, $^{13}C_6$NP, $^{13}C_{12}$Tric, $^{13}C_{12}$BPA and $^{13}C_6$E2) were used as surrogates and a BPC mix containing E1-d4, E2-d4, EE2-d4, MEHP$^{13}C_6$, $^{13}C_6$PBA and $^{13}C_6$MEP was used as an internal standard. The method was validated using recovery of ^{13}C surrogates and spiked samples. The limits of detection ranged from 0.009 to 1.184 ng L^{-1} for particulates and from 0.00065 to 0.11249 μg/kg for soil (Table 2.5).

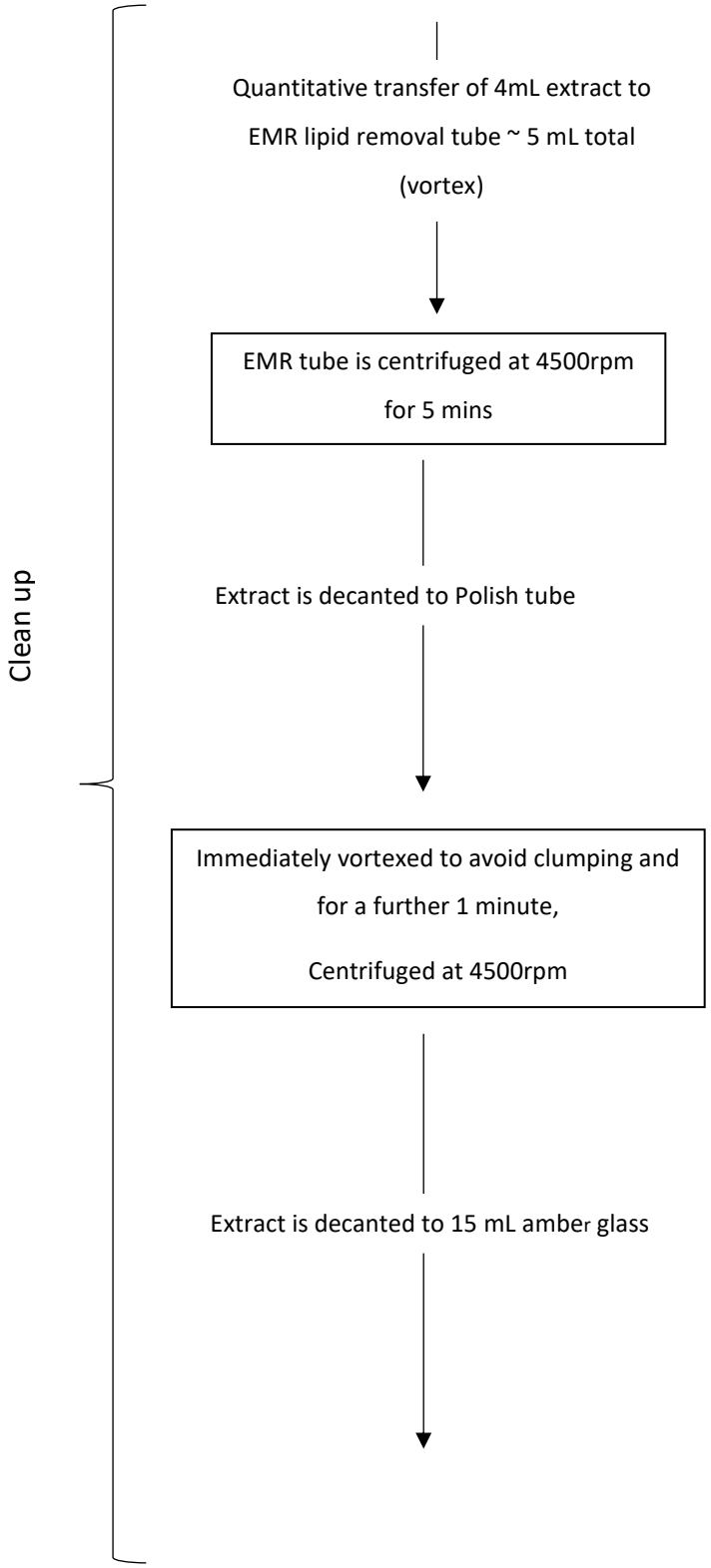
An overview of the method developed for the extraction of soil and particulates is displayed in Figure 2.4, the extraction method involved use of an ultrasonic bath. The clean-up method developed is also displayed within Figure 2.4, and involved use of an EMR clean-up kit with centrifugation for separation. The Method development and validation process is outlined in Chapter 3, section 3.2

2.3.3 QA/QC

In each sample batch a blank, duplicate and spiked sample was included. All samples were spiked with 50 μL of 1 μg ml^{-1} 13C-labeled surrogate mix to determine analyte recovery of the extraction method. Comparative standards were dispensed at the time of spiking corresponding samples to calculate analyte recoveries.

Figure 2.4: An overview of the developed method used for soil, particulates and effluent




Clean up
Quantitative transfer of 4mL extract to EMR lipid removal tube ~ 5 mL total (vortex)
EMR tube is centrifuged at 4500rpm for 5 mins
Extract is decanted to Polish tube
Immediately vortexed to avoid clumping and for a further 1 minute,
Centrifuged at 4500rpm
Extract is decanted to 15 mL amber glass

2.3.4 Limits of Detection

The limits of detection for soil, effluent and particulates were calculated as per EPA Method 8280A. The LOD for each analyte was calculated from the average of three spiked samples for each matrix (Table 2.5).

Table 2.5: Limits of detection (LOD) of analytes in soil, effluent and particulates with ± 95% confidence

Analyte	LOD Soil (μg/kg) ± 95% CI	LOD Effluent (ng/L) ± 95% CI	LOD Particulates (ng/L) ± 95% CI
Androstenedione	0.02743 ± 0.02159	9.673 ± 8.844	1.184 ± 2.105
BPA	0.00363 ± 0.00052	0.849 ± 1.046	0.030 ± 0.014
bParaben	0.00660 ± 0.00413	0.790 ± 1.299	0.027 ± 0.003
BP-1	0.00164 ± 0.00132	0.572 ± 0.728	0.007 ± 0.002
BP3	0.00206 ± 0.00099	0.890 ± 1.445	0.024 ± 0.027
bzParaben	0.00908 ± 0.00187	1.684 ± 0.579	0.050 ± 0.004
Chlorophene	0.00356 ± 0.00227	1.165 ± 1.818	0.017 ± 0.004
Chloroxylenol	0.00065 ± 0.00028	0.025 ± 0.028	0.020 ± 0.011
eParaben	0.00133 ± 0.00013	0.127 ± 0.121	0.197 ± 0.351
E1	0.11249 ± 0.05989	18.89 ± 6.904	0.544 ± 0.129
E2	0.00721 ± 0.00475	0.937 ± 0.434	0.029 ± 0.014
EE2	0.00093 ± 0.00049	0.036 ± 0.009	0.008 ± 0.009
E3	0.00137 ± 0.00117	0.327 ± 0.165	0.023 ± 0.025
17α estradiol	0.02185 ± 0.01942	0.994 ± 0.280	0.741 ± 1.381
4MBC	0.01110 ± 0.00714	3.689 ± 3.924	0.127 ± 0.102
mParaben	0.00105 ± 0.00067	0.066 ± 0.081	0.016 ± 0.009
mTric	0.01791 ± 0.01204	4.012 ± 2.236	0.009 ± 0.082
NP	0.00603 ± 0.00481	2.495 ± 3.884	0.010 ± 0.002
OMC	0.01518 ± 0.00710	11.38 ± 10.34	0.093 ± 0.045
OP	0.01495 ± 0.01318	1.031 ± 1.240	0.223 ± 0.100
OPP	0.00270 ± 0.00095	0.076 ± 0.062	0.129 ± 0.109
3PBOH	0.00939 ± 0.00653	1.525 ± 2.026	0.027 ± 0.008
pParaben	0.00483 ± 0.00212	0.601 ± 0.580	0.025 ± 0.005
Testosterone	0.00168 ± 0.00147	0.107 ± 0.070	0.108 ± 0.196
Tric	0.00884 ± 0.00499	1.708 ± 1.557	0.065 ± 0.025

2.4 Gas Chromatography Mass Spectrometry Analysis

2.4.1 Sample Derivatisation

Prior to analysis, samples were dried under a gentle stream of N_2 using a Techne sample concentrator Dri-Block (DB-3D) set at 40°C until ~ 5 mL of sample remained. The sample was then made up in a 10-mL volumetric flask in ACN enabling the sample to be split. Half of the sample (5 mL) was dried again until complete dryness before being quantitatively transferred using 1 x 500 μL, 2 x 250 μL ACN into 1 mL derivatization vials. Following this 50 μL of the 1 μg mL^{-1} BPC internal standard mix was added and the samples were again reduced to complete dryness under N_2 at 40°C. Following this, vials were left to cool for 10 minutes, 30 μL of the derivatisation mix (MSTFA) was added to each vial, followed by incubation at 65°C for 45 minutes. Samples were cooled for 10 minutes, 970 μL of isooctane was added to each vial before being transferred into GC-MS vials for analysis. Each batch of derivatised samples included a derivatisation blank as well as two check calibration standards a 50 and 250 μg L^{-1}.

Preparation of the MSTFA derivatization mix

The derivatization mix was prepared by adding 11.4 mg NH_4I (ammonium iodide), 17 μL 2-mercaptoethanol and 285 μL of MSTFA (N-Methyl-N-(trimethylsilyl) trifluoroacetamide) to a 1ml reacti vial. The contents were vortexed and incubated at 60-65°C until fully dissolved. The vial was vortexed periodically during incubation. Once the NH_4I was fully dissolved the contents were cooled to room temperature and an additional 2715 μL of MSTFA was added. This was vortexed to homogenise the mixture. The vial was purged with N_2 to exclude air and moisture. The cap was sealed tightly and the mixture was stored in the fridge for up to 10 days. After each use the air space in the vial was purged with N_2.

2.4.2 Instrumental Analysis

Following derivatization, calibration standards and sample extracts were analysed by gas chromatography mass spectrometry (GC-MS). The system comprised of a Shimadzu GC-2010 Gas Chromatograph, interfaced to a Shimadzu AOC-20i Auto Injector and Shimadzu GCMS-

QP2010Plus detector. The software used for instrument control, data acquisition and data processing was performed using the Shimadzu GCMS Solution software (Version 2.70).

The column chosen for separation of analytes was a Rxi-5Sil column (5% diphenyl/95% dimethyl polysiloxane) 30m x 0.25mm ID, 0.25um film thickness, with an integrated guard column (10 m, Integra-Guard) (Restek, Belleftone USA). Derivatised 1 μL samples and calibration standards were injected into the injection port in splitless mode at a temperature of 250°C [115]. The splitless time equalled 1 minute and the split flow rate was 50 – 100 mL per minute. The oven temperature was initially 100°C which was held for 5 minutes, then increased to 300°C at a rate of 10°C per minute, and held for 20 minutes, resulting in a total run time of 45 minutes. The carrier gas helium was used at a flow rate of 5.5 mL min^{-1}. The ion source was held at 200°C and the GC-MS interface at 250°C. The MS was calibrated against perfluorotributylamine (PFTBA) after routine maintenance such as cutting of the column or changing of the glass liner. The retention times and m/z ratios used for the detection and quantification of internal standards, 13C surrogates and target compounds are presented in Table 2.6 and Table 2.7. This method was based on the method developed and validated by Lisa Graham [118].

Table 2.6: Retention times and detection parameters of internal standards and 13C surrogates (Ordered for retention times)

Analyte	Rt(min)	Quantifier ion *(m/z)*	Qualifier ions *(m/z)*
13C16 mParaben	12.656	215	230
13C6 mEP*	14.169	255	227, 181
13C6 bParaben	16.061	216	201, 199
13C6 NP	17.745	185	186, 298
13C6 3-PBA*	18.05	277	233, 203, 292
13C6 mEP*	14.169	255	227, 181
mEHP 13C6*	19.57	225	227, 153, 243
13C12 Tric	19.827	206	257, 359
13C12 BPA	20.545	369	370
BPC*	21.018	385	386, 400
E1-d4	24.163	346	257, 285
E2-d4	24.278	420	287, 421
13C6 E2	24.46	288	422, 332
EE2-d4	25.49	429	430, 444

Table 2.7: Retention times and detection parameters of target analytes (Ordered for retention times)

Analyte	Rt(min)	Quantifier ion *(m/z)*	Qualifier ions *(m/z)*
Chloroxylenol	11.351	213	228, 177, 215
mParaben	12.534	224	209, 177, 193
eParaben	13.497	238	223, 193, 210
OPP	14.062	211	227, 242
OP	14.458	207	208, 191, 151
pParaben	14.832	207	208, 191, 193
bParaben	15.94	195	210, 193, 266
3PBOH	16.954	183	227, 272, 257
Chlorophene	17.549	275	290, 165
NP	17.618	292	180, 165
4MBC	19.148	254	155, 239
BP3	19.265	285	286, 242, 223
mTric	19.688	252	302, 254, 232
Tric	19.702	360	362, 310
BP-1	19.831	343	347, 164, 270
bzParaben	20.125	193	300, 85
BPA	20.419	357	385, 372, 171
OMC	21.364	178	161, 133, 290
17α Estradiol	23.987	416	285, 129
E1	24.065	342	218, 244, 327
Androstenedione	24.182	430	432
E2	24.315	416	285, 129
Testosterone	24.32	432	285, 417
EE2	25.162	425	285, 232, 218
E3	25.733	504	345, 386, 414

2.4.3 Calibration Curve

A set of calibration standards (1000, 500, 250, 100, 50, 25, 10, 5, 2.5 and 1 μg mL^{-1}) were prepared by adding appropriate amounts of the native mix and ^{13}C surrogate mix and 50 μL of 1 μg mL^{-1} BPC internal standard mix to derivatization vials. Calibration standards were reduced to dryness under a gentle stream of N_2 at 40 °C. The calibration standards were derivatized as described in section 2.4.1. A fresh set of calibration standards was prepared every second day with check standards run daily. During the derivatization step it was important to ascertain that the temperature was 65°C for the entire 45-minute incubation period. This was seen to be particularly important for chloroxylenol.

2.4.4 Instrumental QA/QC

To maintain ideal instrumental analysis conditions, several quality control practices were implemented. Before analysis of each batch the rinse vials containing iso-octane, toluene and dichloromethane were changed. The injection needle was also cleaned thoroughly with dichloromethane: methanol 95:5. Ensuring the injection needle was thoroughly cleaned was crucial in ensuring an uninterrupted analysis sequence due to crystals forming in the samples during derivatization. Duplicate injections of standards were performed after every 10 samples to ensure there was no reduction in signal response. Before and after each sample injection, the syringe was programmed to rinse three times each with iso-octane, methanol and dichloromethane. At the end of each sample sequence at least two iso-octane blanks were injected to condition the column thus flushing any volatiles from the system which may have accumulated. Before the following run the chromatogram of these blanks were checked to ensure any background noise was at an acceptable level. At the beginning of each sample sequence an iso-octane blank was injected as a sample to ensure the column was clean.

Following the replacement of the glass liner, one standard and at least four environmental samples were injected and run as samples to ensure active sites within the injection port were occupied and stabilised.

2.4.5 Determining Limits of Detection

Limits of detection (LOD) for all analysis carried out by gas chromatography in this thesis were calculated using EPA Method 8280A. The equation below was used to calculate the LOD.

Equation 2: Limits of detection

$$LOD = \frac{2.5 \times Cis \times Hn \times C}{His \times RF}$$

Cis = Concentration of internal standard in sample

Hn = Peak height of noise for the target ion near the target analytes retention time.

C = Concentration factor, this is calculated based upon the volume of the sample extracted and the volume concentrated down to prior to analysis.

His = Peak height of the internal standard

RF = Response factor, ratio of the area of target analyte to the internal standard, multiplied by the ratio of concentration of internal standard to the lowest concentration of calibration standard in which the target analyte can be detected, see equation below.

Equation 3: Response factor

$$RF = \frac{Area\ of\ target\ analyte\ (sample)}{Area\ of\ internal\ standard\ (sample)} \times \frac{Concentration\ of\ internal\ standard\ (lowest\ calibration\ standard)}{Concentration\ of\ analyte\ (lowest\ calibration\ standard\ that\ can\ be\ detected)}$$

2.4.6 Silanization of glassware

Silanization is an important process used to treat glass surfaces to ensure that target compounds are unable to adhere to the surface of the glass. This process was completed for the reacti vials used for drying down samples and sample derivatisation.

Firstly, glassware was cleaned thoroughly by rinsing with 3 x methanol, 3 x acetonitrile and 3 x acetone, it was then allowed to air dry inverted on tissue paper in a fume hood. A solution of 5% dimethyldichlorosilane in toluene was prepared in a 500-mL glass beaker, glass reacti vials were introduced into the beaker and shaken slightly by hand for 10 minutes. Vials were then rinsed with toluene, methanol, toluene and again methanol. Vials were then dried for 20 minutes at 80°C in a drying oven.

2.5 Total Suspended Sediment Analysis (TSS)

From each groundwater and effluent site 1L samples were collected in amber glass bottles with Teflon lined lids for the analysis of TSS, a duplicate was collected on each sampling trip. Samples were filtered through pre-cleaned dried and weighed Whatman GF/C 47mm filter papers, dried in a drying oven at 105°C for an hour, allowed to cool in a desiccator and re-weighed to calculate the TSS (Equation 4).

Equation 4: Total suspended sediments

$$Total\ Suspended\ Solids\ \left(\frac{mg}{L}\right) = \frac{(A-B)*1000}{C}$$

Where: A = weight of filter and solid in mg

B = weight of filter in mg

C = volume of sample filtered in mL

2.5.1 QA/QC

Each sampling event included a sample duplicate to account for variation, the % difference values are reported in Table 2.8. The percentage differences between samples were relatively high ranging from 0% to 200%, these high differences indicate that this method was very variable, this can most likely be attributed to the varying nature of groundwater samples. Collection of a single 2L sample and splitting before analysis in the lab may reduce this variance.

Table 2.8: Percentage difference for total suspended sediment in duplicate groundwater samples

Sample	% difference
W12, W12 duplicate	64.1%
W33, W33 duplicate	66.7%
W44, W44 duplicate	200%
W13, W13 duplicate	0%
W18, W18 duplicate	200%
W13, W13 duplicate	47.6%
W12, W12 duplicate	10.8%
W44, W44 duplicate	200%
W71, W71 duplicate	51.9%
W15, W15 duplicate	25.8%
W24, W24 duplicate	0%

2.6 Dissolved Organic Carbon Analysis – Groundwater and Effluent

Groundwater and effluent samples were analysed for dissolved carbon and dissolved inorganic carbon at the University of Canterbury's Special Purposes Laboratory, Department of Engineering. The samples were analysed using the Shimadzu TOC-L CSH analyser equipped with Shimadzu ASI-L auto sampler. The Shimadzu TOC-L CSH analyser had a working range of 4 μg/L to 30,000 mg/L.

Instrumental Analysis

Following filtration of 1L samples through Whatman GF/C 47 mm filter papers, samples were transferred into 8 mL glass vials. Samples were analysed using the Shimadzu TOC-L CSH analyser interfaced to a Shimadzu ASI-L auto sampler. The software used for instrument control was performed using TOC-control v1.01 software.

Calibration Curve

The instrument was calibrated for dissolved carbon (DC) by preparing a stock solution at a concentration of 1000 mg/L total carbon. This solution was made up by dissolving 2.125 grams of potassium hydrogen phthalate in 1000 mL of Ultrapure Milli-Q water. A series of dilutions were then carried out to give the following solutions 0, 5, 10, 25, 50 and 100 mg/L. Before making the standard stock for DC calibration, the potassium hydrogen phthalate was dried at 110°C for one hour and cooled in a desiccator to prevent weighing inaccuracies.

The instrument was calibrated for dissolved inorganic carbon (DIC) by making up a stock solution at a concentration of 1000 mg/L dissolved inorganic carbon. This solution was made up by dissolving 3.497 grams of sodium bicarbonate and 4.412 grams of sodium carbonate in 1000 mL of Ultrapure Milli-Q water. A series of dilutions were then carried out to give the following solutions 0, 5, 10, 25, 50 and 100 mg/L.

Prior to making the standard stock for DIC calibration, sodium hydrogen carbonate was dried overnight in a desiccator and sodium carbonate was dried in an oven at 250°C for an hour, also to prevent weighing inaccuracies.

2.7 Total Organic Carbon Analysis - Soil

Total organic carbon analysis was carried out for the collected soil samples. Total carbon and inorganic carbon were analysed at the University of Canterbury's Special Purposes Laboratory, Department of Engineering. The samples were analysed using the Shimadzu SSM-5000A analyser with TOC-control L v.01 software.

Sample Preparation and Calibration

Prior to analysis soil samples were dried in a drying oven at 105°C for 24 hours. The soil was then crushed in a mortar and pestle to ensure a uniform sample.

The instrument was calibrated for total carbon (TC) by weighing out 20 mg and 40 mg amounts of sucrose (42% carbon) in tared weigh boats and analysing like samples to produce a calibration curve.

The instrument was calibrated for total inorganic carbon (TIC) by weighing out 20 mg and 40 mg amounts of sodium bicarbonate (14.29% carbon) in tared weigh boats and analysing like samples. Each sample run included new calibration standards. Prior to loading samples for analysis sample boats were cleaned with ultrapure MilliQ water and heated to 900°C in the instrument to ensure sample boats were free of any residual carbon from previous samples.

2.8 Moisture content for soil

The moisture content of each soil sample was calculated by taking a sub sample of at least 40 grams of soil. This was weighed into an aluminium dish and dried for 24 hours in a drying oven at 105 °C. The sample was then allowed to cool in a desiccator and reweighed. Equation 5 was used to calculate the soil moisture content.

Equation 5: Moisture content of sample

$$MC\% = \frac{W_2 - W_3}{W_3 - W_1} \times 100$$

W_1= Weight of weighing tin only

W_2= Weight of moist soil and tin

W_3= Weight of dried soil and tin

2.9 Cleaning of glassware and equipment

All glassware used for analysis of EOCs, including sample containers and lab equipment was solvent rinsed prior to use with three times MeOH, three times ACN and three times acetone. The Teflon transfer lines for solid phase extraction were cleaned thoroughly by passing through 10 mL of each solvent three times (MeOH, ACN and acetone) consecutively, the outside of the teflon tubing was wiped using methanol.

All glassware used for organic carbon analysis including sample bottles, and glassware were soaked in hot water with decon 90, then rinsed in hot water 3 times followed by 3 rinses in Milli-Q water.

All glassware used for total suspended sediment analysis including sample bottles and laboratory glassware were soaked in hot water with decon 90, then rinsed in hot water followed by 3 rinses in Milli-Q water.

CHAPTER THREE

SOURCES OF EOCs TO GROUNDWATER & DEVELOPMENT OF A NOVEL METHOD FOR THEIR EXTRACTION FROM SOIL AND PARTICULATES

3 Sources of EOCs to Groundwater & Development of a Novel Method for their Extraction

3.1 Introduction

Sources of EOCs to the environment can be divided into point source and diffuse sources of pollution. An overview of the major sources of EOC pollution to groundwater is presented Figure 3.1. Emerging organic contaminants enter the environment through several sources and pathways, it is well recognized that the range of contaminants present in groundwater are driven by anthropogenic activities occurring at the surface [119].

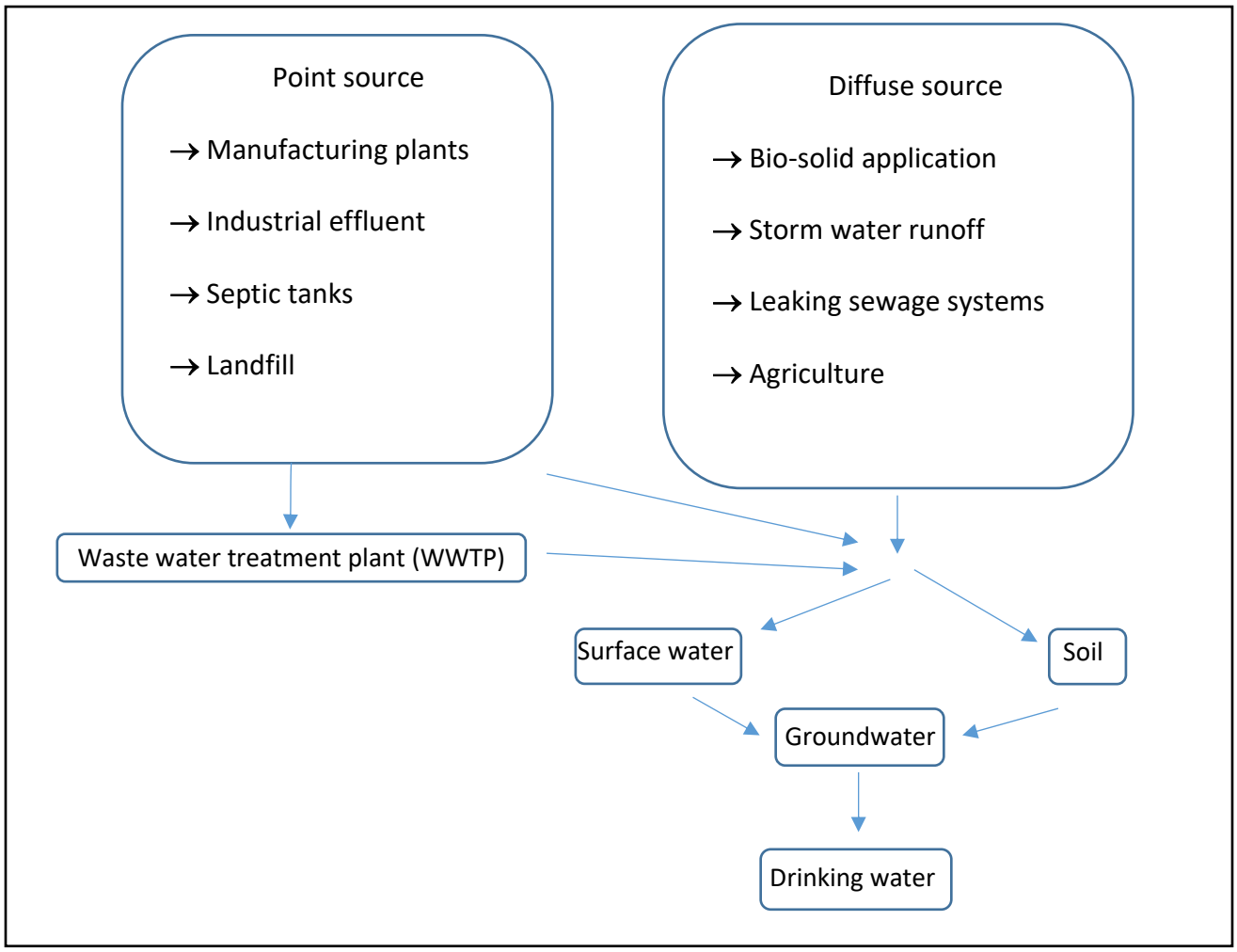


Figure 3.1: Origin and routes of emerging contaminants to groundwater

Point source pollution originates from a single identifiable source from a distinct location [120]. Important point sources of EOCs include, wastewater treatment plants, manufacturing plants, industrial discharges, septic tanks, concentrated animal feeding operations, accidental spills and landfill leaching. In comparison, diffuse pollution originates from diffuse sources over a broad area and often cannot be recognized with a single discharge source [121]. Some examples of diffuse sources of EOCs include runoff from bio-solids and manure application, storm water runoff, leakage from sewage tank systems and agriculture which is the main non-point source polluter of groundwater [122]. As non-point source contaminants are applied over large areas they can have a greater impact on groundwater quality compared to point sources. At present many published studies investigating EOCs have focused on groundwater contamination due to point sources [123], this is most likely because point source discharges are easier to manage or control and therefore provide greater environmental benefits. Waste water treatment plant effluent is one of the key point sources of EOCs to the environment [124]. Wastewater effluent can contain a wide variety of contaminants, including personal care products (PCPs), pharmaceuticals, fragrances, cleaning products and household detergents, plant and animal steroids, fragrances and flavourings. Land disposal of waste water treatment plant effluent is a very common practice in New Zealand in rural areas [125]. This practice allows percolation of contaminants through the soil and into groundwater, contamination can also occur through groundwater surface-water exchange by the contamination of surface water bodies [126].

In Canterbury one of the major sources of EOCs to groundwater is thought to be the application of wastewater to land. The purpose of this study was to collect samples from potential sources of EOCs in Canterbury, including farm effluent, WWTP effluent and soils irrigated with these wastes and analyse for a suite of EOCs.

To analyse these samples there was a need to develop a cost-efficient method for their extraction and clean-up. There are a range of techniques already used for the extraction of EOCs from solid samples however many of these have drawbacks due time efficiency, large solvent requirements and cost. Common extraction procedures include Soxhlet extraction [127], pressurized liquid extraction [128], microwave assisted extraction [129], and ultrasonic assisted extraction. These

extraction methods are generally followed by solid phase extraction (SPE) which is used for purification and preconcentration of samples.

Soxhlet extraction involves refluxing of samples in solvent and requires boiling, rinsing and recovery of the solvent therefore is time consuming [130]. Soxhlet also requires a large volume of organic solvents [131] and has been criticized by researchers for its difficulty in reproducing results [132]. Pressurized liquid extraction (PLE) is a technique using liquid solvents at elevated temperature and pressure [133]. Pressurized liquid extraction (PLE) does have a few advantages over traditional techniques such as Soxhlet extraction and ultrasonic assisted extraction in that the extraction time is short and little solvent is consumed [134]. However, disadvantages of PLE include lack of selectivity towards analytes during extraction and dilution of analytes when a high number of cycles is used [135]. Microwave assisted extraction (MAE), utilises microwave energy to heat up the solvent which is in contact with the solid sample to promote partitioning of analytes from the sample into the solvent [129]. One of the main advantages of MAE is the significant reduction in solvent required thus reducing waste and extraction time, however microwave assisted extraction requires specialist equipment which can be costly. Ultrasonic assisted extraction (UAE) uses ultrasound waves which create voids or bubbles in the liquid, these implode causing high temperature and pressure locally, this force results in transfer of material into the solvent [136]. Ultrasonic assisted extraction is frequently used in the analysis of environmental samples producing results comparable with that of accelerated solvent extraction for sewage sludge and soil [137]. The main benefit of ultrasonic assisted extraction is the high throughput due to multiple samples being able to be extracted at one time and it is also very cost effective.

In the present study, an ultrasonic assisted extraction was developed for the extraction of soil and particulate samples followed by sample clean-up using an Enhanced Matrix Removal (EMR) lipid clean up and polish kit manufactured by Agilent. EMR – Lipid contains a unique proprietary sorbent which selectively removes lipids from complex matrixes without the removal of analytes. The polish step contains $MgSO_4$ which improves removal of water and nonmatrix solid residue. Removal of water is important for GC applications having a significant impact on analyte response, peak shape, and more consistent reproducibility between injections. This EMR clean

up and polish was also trialled on the effluent samples following solid phase extraction, the final method is described in section 2.3. The usual method of clean-up for effluent samples would be Gel Permeation Chromatography (GPC) as described in Philipp Emnet's thesis [115]. However, this method is not available at the University of Canterbury and due to the small number of samples clean-up was performed using dispersive SPE EMR lipid removal followed by a polish step.

3.1.1 Objectives

The specific objectives of Chapter Three were to:

- Identify potential sources of EOCs to groundwater in Canterbury
- Develop a novel method for the extraction of soil and particulates and clean-up of soil, particulates and effluent samples to be analysed for EOCs
- Determine if EOCs were present in a range of effluent and soil samples collected from across Canterbury

3.2 Method

Development and Validation

The method was initially trialled by spiking 10 mL of acetonitrile with 50 μL of the 1ppm native mix. The extracts were then cleaned up using EMR. Differing amounts of ultrapure water (2.5 and 5 mL) were added to the sorbent of the EMR tube for activation of the sorbent to determine the effect on recoveries. This process identified that 2.5mls of water achieved better recoveries (Table 3.1). There was an interference at the same retention time as chloroxylenol, which resulted in not being able to quantify this peak. The GC-MS temperature profile was modified to try separate out the interference but was not successful. The spike recovery experiment was repeated a second time using 1, 2, 2.5 and 5 ml of ultrapure water to determine if less water would improve recoveries. The 2.5ml still showed the best recoveries, with recoveries ranging largely between 65-99%. A few compounds fell outside of this range including mParaben, NP, E2, E3 and testosterone with recoveries ranging from 43-62% (Table 3.1).

For further method validation, the extraction efficiency was tested in triplicate. Five grams of Ottawa sand was weighed into 50ml glass centrifuge tubes, 10 mL of acetonitrile was added followed by 50 μl of the 1ppm native mix. The tubes were placed in an ultrasonic bath for 10 minutes at room temperature with the sweep function selected. Following ultrasonication, the tubes were centrifuged at 3000 rpm for 5 minutes; the extract was decanted and the process was repeated twice more with 10 mL of ACN. The 30ml extracts were dried down to approximately 5 mL under a gentle stream of N_2 at 40 °C this took approximately 6 hours. Extracts were 'cleaned up' by firstly adding 2.5 ml of water to the EMR lipid tube for activation. The 5 ml extracts were then added, vortexed and centrifuged at 4500 rpm for five minutes. The supernatant was then transferred to the polishing tube, vortexed immediately and for an extra minute and centrifuged at 4500 rpm for 5 minutes. The upper acetonitrile layer was transferred to sample vials and analysed by GC-MS (section 2.4). The recoveries for the complete process using Ottawa sands ranged from 64-136% with the exception of nonylphenol with a recovery of 35% (Table 3.2).

As overall acceptable recoveries were achieved except for chloroxylenol which displayed interferences, the entire process was repeated using uncontaminated soil samples. Five-gram soil samples were weighed along with five-grams of Ottawa sand, and spiked with 50 μL of the 1 ppm native mix, blank soil samples were also included. The above process was repeated as for the Ottawa sands. The average recoveries mainly ranged from 76-157%, nonylphenol still showed a lower recovery of 61%. A few compounds had high recoveries which did not fit within the acceptable range, these compounds included OPP, bzParaben and E1, with recoveries of 261%, 186% and 220% respectively.

Method validation was further validated by repeating the above soil extraction and clean-up with the addition of 13C surrogate compounds. This was achieved by adding 50 μL 1 μg mL^{-1} 13C surrogate mix to each sample extract before extraction and clean-up. During this run the amount of ultrapure water added for activation of the EMR tubes was altered to 1.5 mL to reflect the moisture content that was already present from the soil. The recoveries achieved with the addition of only 1.5 mL of water were much lower than the previous addition of 2.5 ml. As a result, 2.5 ml was used for the final method. Average soil recoveries using 2.5 mL ultrapure water mainly ranged from 70-134% (n=2), a few compounds which fell outside of this range included 3PBOH, NP, BP3, E3 and Androstenedione with recoveries of 64%, 26%, 61%, 58% and 47% respectively (Table 3.3). OP and E1 had extremely high recoveries which is likely due to a derivatization issue.

Table 3.1: Percentage recoveries of target analytes with varying amounts of ultrapure water (5, 2.5,2 and 1 mL) used for activation of EMR (n=2)

Analyte	% Recovery (5 mL)	% Recovery (2.5 mL)	% Recovery (2 mL)	% Recovery (1 mL)
Androstenedione	10.4	67.2	79.1	55.3
BPA	14.3	80.2	75.9	54.4
bParaben	14.4	76.1	69.0	46.4
BP-1	13.3	91.6	78.2	55.7
BP3	17.9	77.1	70.1	50.5
bzParaben	21.2	97.3	87.0	59.0
chlorophene	21.4	76.2	68.1	55.8
chloroxylenol	NQ	NQ	NQ	NQ
eparaben	14.4	65.5	67.8	49.4
E1	14.3	99.1	72.1	63.9
E2	13.8	62.6	65.3	52.5
EE2	8.1	71.4	72.5	54.5
E3	28.3	43.5	67.8	59.1
17α Estradiol	10.6	71.9	70.0	50.8
4MBC	16.4	76.9	66.5	41.0
mparaben	10.7	51.4	62.0	43.6
mTric	22.9	84.2	68.1	46.4
NP	8.2	56.8	29.1	25.9
OMC	13.9	88.9	65.2	54.3
OP	23.5	75.6	63.7	40.4
OPP	7.3	70.2	42.2	13.6
3PBOH	15.2	67.7	64.3	48.8
pParaben	21.1	74.9	68.3	46.3
Testosterone	7.0	62.2	71.7	52.4
Tric	22.3	86.6	79.1	56.6

NQ= Not quantifiable due to an interference on chromatogram

Table 3.2 Average recoveries of target analytes extracted from five grams of Ottawa sand (n=3)

Analyte	% Recovery n=3
Androstenedione	95.6
BPA	136.5
bParaben	77.7
BP-1	98.4
BP3	77.1
bzParaben	94.9
Chlorophene	80.2
Chloroxylenol	NQ
eParaben	86.1
E1	113.4
E2	77.2
EE2	85.8
E3	79.2
17a Estradiol	82.4
4MBC	92.4
mParaben	84.2
mTric	79.3
NP	34.8
OMC	81.2
OP	86.3
OPP	99.9
3PBOH	76.9
pParaben	63.9
Testosterone	87.1
Tric	81.5

NQ= Not quantifiable due to an interference on chromatogram

Table 3.3 Average recoveries of target analytes and 13C surrogates from spiked soil using 2.5 mL ultrapure water for EMR activation

Analyte	% Recovery n=2	Surrogates	% Recovery n=2
Androstenedione	46.7	BPA (ring 13C12)	78.1
BPA	92.3	bParaben (ring 13C6)	81.5
bParaben	76.6	E2 (ring 13C6)	89.7
BP-1	114.9	mParaben (ring 13C6)	88.0
BP3	61.6	NP (ring 13C6)	30.2
bzParaben	100.3	Tric (ring 13C12)	75.8
chlorophene	77.6		
chloroxylenol	NQ		
eparaben	98.8		
E1	524.2		
E2	85.1		
EE2	134.2		
E3	58.2		
17α Estradiol	86.8		
4MBC	101.8		
mparaben	92.2		
mTric	64.1		
NP	26.3		
OMC	87.4		
OP	406.9		
OPP	91.4		
3PBOH	63.9		
pParaben	69.6		
Testosterone	74.2		
Tric	70.5		

NQ= Not quantifiable due to an interference on chromatogram

3.2.1 Sampling - Sources of EOCs

Soil Sampling

Soil was sampled at sites which were irrigated with either effluent from a wastewater treatment plant or dairy shed (Table 3.4).

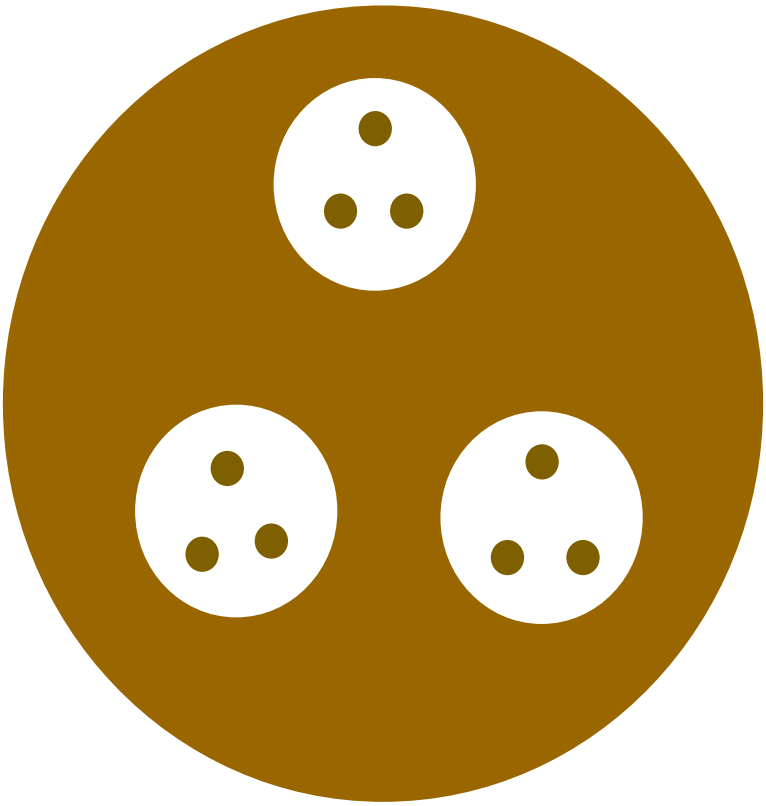
Table 3.4: Summary of sampling locations of soil

Site	Receives
S1	Wastewater
S11	Wastewater
S2	Wastewater
S22	Wastewater
S3	Dairy shed effluent
S4	Dairy shed effluent

Soil cores were collected using a stainless-steel push sampler after laying down a 3-foot sampling ring. Three equally spaced soil cores were retrieved from within each ring to form a composite sample of 9, sample cores were collected from the surface to a depth of approximately 100mm, this depth was predetermined by the stainless-steel push sampler (Figure 3.2). Samples were collected into clear snap lock bags which were double bagged and stored in a chilly bin containing ice packs.

Soil samples were extracted and analysed in duplicate, the average concentration of the sample and the duplicate was reported, where an analyte was not detected in both the sample and duplicate the average of the two was calculated. Any analytes detected in the blanks were subtracted from the analytes concentration in the samples. There were minimal concentrations of contamination in the blanks, low concentrations of BPA were the only contaminant present in the solvent blank.

Figure 3.2: Sampling pattern used to collect soil samples



Effluent Sampling

Effluent from three WWTPs and effluent from two dairy sheds were collected (Table 3.5). Samples were collected as grab samples in an 8L stainless steel bucket and immediately transferred to solvent rinsed 4 L amber bottles. Samples were transported back to the laboratory on ice and immediately acidified using concentrated sulphuric acid to a pH ~ 2. Samples were filtered through GF/C filter papers with a layer of celite, to aid the filtration process. The dairy shed effluent collected from site DS2 was unable to be filtered due to extremely high amounts of organic matter, instead this sample was freeze dried along with calculation of its moisture content, and extracted in the same way as soil. Following filtration effluent samples were extracted by solid phase extraction within 48 hours.

Effluent samples were extracted and analysed in duplicate, the average concentration of the sample and the duplicate was reported, where an analyte was not detected in both the sample and the duplicate the average of the two was calculated. Any analytes detected in the blanks were subtracted from the analytes concentration in the samples. There were very low concentrations of contamination in the cartridge blanks, low concentrations of BPA were the only contaminant present in the cartridge blank for all 5 of the effluent batches. However, the cartridge blank extracted alongside effluent sample WW2 also contained contamination from OPP, pPara, and 3PBOH, these were all at background concentrations ranging from 2.7-3.1 ng/L, these were corrected for in sample WW2. Full data on analysis of blanks are available in the Appendix, (Table 8.12).

Table 3.5: Summary of effluent sampling locations across the Canterbury region.

Site	Location	Effluent Type	Sample Point
WW1	Amberley	WWTP effluent	Buffer pond
WW2	Ashburton	WWTP effluent	Effluent prior to treatment
WW3	Akaroa	WWTP effluent	After final treatment
DS1	Lincoln	Dairy shed effluent	Dairy shed sump
DS2	Oxford	Dairy shed effluent	Oxidation Pond

3.3 Results and Discussion

3.3.1 Analytical Method Performance – Effluent, Soil and Particulates

To determine the performance of the developed method surrogate and analyte spike recoveries were quantified against the comparative standard. The recovery data is presented below in Table 3.6 for effluent spiked samples, Table 3.8 for soil spiked samples and Table 3.10 for particulate spiked samples.

Effluent

Average recoveries for effluent (mean ± confidence interval, n = 5) were 127% ± 54%, 69% ± 31%, 27% ± 16%, 79% ± 26% and 83% ± 13% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 correspondingly (Table 3.7). The overall average recoveries were mostly acceptable with the exemption of $^{13}C_6$-NP with an average recovery of 27%, this low recovery for $^{13}C_6$-NP is thought to be caused by its lipid like structure as the clean-up process removes long chain fatty acids. Although the overall averages are high the 95% confidence interval values are very high, due to the high standard deviations of the recoveries, this indicates a great variability of surrogate recoveries between different samples. This variability between samples is likely caused by several factors, such as, a complex sample matrix of natural organic material (NOM) due to insufficient clean-up of samples prior to analysis. Variability may also be caused by SPE extraction variability, as each sample was extracted on different days.

Average recoveries for most of the target analytes ranged from 62%-186%, except for E1 and androstenedione with recovery values of 911% and 30% respectively (Table 3.6). The extremely high and low recoveries for E1 and Androstenedione respectively are most likely due to a derivatization issue and a potential conversion between the two compounds [138]. Chloroxylenol was unable to be quantified due to an interference at the retention time in the chromatogram. Due to issues in recoveries and interferences, E1, androstenedione and chloroxylenol are not included in the data analysis of effluent samples.

Table 3.6 Spike recoveries and statistical summary of analytes from 1L effluent samples (n=5)

Analyte	Average % Recovery 1L effluent n=5	Std Dev	95% C.I.
***Androstenedione**	29.4	34.6	30.3
BPA	121.6	385.7	338.0
bParaben	148.4	314.1	275.3
BP-1	168.4	201.6	176.7
BP3	118.0	128.6	112.7
bzParaben	88.3	57.1	50.0
chlorophene	121.8	78.0	68.4
***chloroxylenol**	-	-	-
eparaben	177.3	89.5	78.4
***E1**	911.5	692.8	607.2
E2	84.6	25.0	22.0
EE2	62.5	37.5	32.9
E3	119.2	140.7	123.3
17α Estradiol	81.7	25.2	22.1
4MBC	168.1	39.5	34.6
mparaben	175.0	150.1	131.6
mTric	102.3	25.4	22.3
NP	72.9	88.8	77.8
OMC	89.6	94.7	83.0
OP	186.0	228.4	200.2
OPP	142.9	25.1	22.0
pParaben	124.5	95.2	83.5
3PBOH	121.7	61.4	53.8
Testosterone	62.0	33.5	29.3
Tric	93.4	46.3	40.6

* Androstenedione, chloroxylenol and E1 were excluded from analysis due to unacceptable recoveries

Table 3.7: Spike recoveries and statistical summary of 13C labelled surrogates from 1L effluent samples (n=5)

Surrogate	Average % Recovery 1L groundwater n=5	Std Dev	95% C.I.
13C12 BPA	83.8	14.3	12.5
13C6 bParaben	68.9	36.2	31.7
13C6 E2	113.0	39.6	34.7
13C16 mParaben	126.8	61.4	53.9
13C6 NP	27.7	18.2	16.0
13C12 Tric	79.2	29.2	25.6

Soil

Average recoveries for surrogates in soil (mean ± confidence interval, n = 5) were 71% ± 7%, 111% ± 9%, 76% ± 11%, 80%, 6%, 58% ± 4% and 54% ± 4% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively (Table 3.9). The average recovery of surrogates was acceptable, however recoveries of 58% and 54% for $^{13}C_{12}$-BPA and $^{13}C_6$-E2 are reasonably low, the data however is less variable as seen by low confidence intervals ranging from 4%-11%. The recovery of most of the target analytes in soil n=5 ranged from 70% - 137% (Table 3.8) with the exception of OPP and E1 with recoveries of 255% and 239%, these high recoveries are thought to be due to a derivatisation issue which meant their recovery values are erroneous. Chloroxylenol showed interferences within the sample chromatogram therefore was not included. Due to issues with recoveries and interferences, OPP, E1 and chloroxylenol were not included in the analysis of soil samples

Table 3.8: Spike recoveries and statistical summary of analytes from soil samples (n=5)

Analyte	Average % Recovery soil n=5	Std Dev	95% C.I.
Androstenedione	71.1	30.2	34.2
BPA	117.8	4.5	5.1
bParaben	93.6	2.2	2.5
BP-1	118.2	11.2	12.7
BP3	97.5	8.8	9.9
bzParaben	88.3	8.2	9.3
chlorophene	91.5	4.5	5.1
***chloroxylenol**	-	-	-
eparaben	132.5	11.7	13.2
***E1**	238.7	125.5	142.0
E2	82.2	5.3	6.0
EE2	91.9	18.2	20.6
E3	73.3	8.0	9.1
17α Estradiol	87.1	12.1	13.7
4MBC	133.4	7.3	8.2
mparaben	137.4	9.7	11.0
mTric	101.7	5.1	5.7
NP	70.2	8.0	9.0
OMC	108.2	9.2	10.4
OP	129.3	13.8	15.7
***OPP**	254.6	16.4	18.5
3PBOH	97.8	3.6	4.1
pParaben	78.2	6.5	7.4
Testosterone	86.5	24.3	27.5
Tric	95.1	6.0	6.7

* Chloroxylenol, E1 and OPP were excluded from analysis due to unacceptable recoveries

Table 3.9: Spike recoveries and statistical summary of 13C labelled surrogates from soil samples (n=5)

Surrogate	Average % Recovery Soil n=5	Std Dev %	95% C.I.
13C12 BPA	58.0	5.9	3.9
13C6 bParaben	110.7	13.4	8.7
13C6 E2	53.9	5.7	3.7
13C16 mParaben	71.0	10.6	6.9
13C6 NP	75.9	17.1	11.2
13C12 Tric	79.8	8.7	5.7

Particulates

Average recoveries for particulates (mean ± confidence interval, n = 7) were 80% ± 12%, 77% ± 11%, 45% ± 14%, 73% ± 9%, 83% ± 12% and 95% ± 24% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 correspondingly (Table 3.11). The average recovery of surrogates was good excluding $^{13}C_6$-NP with a recovery of 45%. Reasonably low confidence intervals for all surrogates except $^{13}C_6$-E2 provided a good indication that the data produced was consistent. The average recovery of target analytes was also reasonable, ranging mainly from 66% to 121% for all analytes except OPP, NP and E1 (Table 3.10). This result was not surprising due to an already apparent issue seen with the derivatisation of OPP and E1 and the structure of NP being like that of a lipid and thus theoretically being removed during clean-up. Chloroxylenol showed interferences within the sample chromatogram therefore was not included. Due to issues in recoveries and interferences OPP, NP, E1 and chloroxylenol were not included in the analysis of particulate samples.

Table 3.10: Spike recoveries and statistical summary of analytes and from particulate samples (n=7)

Analyte	Average % Recovery particulates n=7	Std Dev	95% C.I.
Androstenedione	76.7	57.3	42.5
BPA	91.9	32.2	23.8
bParaben	85.4	16.2	12.0
BP-1	121.1	21.7	16.1
BP3	82.1	16.3	12.1
bzParaben	103.7	24.4	18.1
chlorophene	77.5	13.1	9.7
***chloroxylenol**	-	-	-
eparaben	84.6	19.0	14.0
***E1**	342.9	300.9	222.9
E2	80.2	10.4	7.7
EE2	83.2	11.1	8.2
E3	65.6	22.2	16.5
17α Estradiol	68.5	13.7	10.2
4MBC	96.9	29.2	21.7
mparaben	83.0	26.2	19.4
mTric	82.2	28.8	21.3
***NP**	42.1	17.5	13.0
OMC	90.5	31.9	23.6
OP	81.5	36.7	27.2
***OPP**	56.0	58.3	43.2
3PBOH	77.9	15.3	11.4
pParaben	71.3	14.6	10.9
Testosterone	94.0	49.6	36.8
Tric	74.5	17.6	13.0

* Chloroxylenol, E1, NP and OPP were excluded from analysis due to low recoveries

*Table 3.11***:** *Spike recoveries and statistical summary of 13C labelled surrogates from particulate samples (n=7)*

Surrogate	Average % Recovery particulates n=7	Std Dev %	95% C.I.
13C12 BPA	82.6	16.2	12.0
13C6 bParaben	77.2	15.7	11.6
13C6 E2	94.6	32.8	24.3
13C16 mParaben	80.3	16.7	12.4
13C6 NP	45.0	19.0	14.1
13C12 Tric	73.4	13.2	9.7

3.3.2 Soil parameters

Moisture content of soil

The moisture content of S2 and S22 were high ranging from 65.8% - 93.7% due to recent rain (Table 3.12).

Organic Carbon Content of soil

The TIC concentration for all soil samples were low meaning most of the carbon present was organic carbon. The total organic carbon for all six soil samples ranged from 2.57%-5.29% (Table 3.12).

Table 3.12: Moisture content, total Carbon, total inorganic carbon and total organic carbon from each soil sample

Soil Site	Moisture Content	Total Carbon	Total Inorganic Carbon	Total Organic Carbon
S1	28.5%	5.3%	<0.1%	5.3%
S11	5.6%	3.4%	<0.1%	3.4%
S2	65.8%	2.6%	<0.1%	2.6%
S22	93.7%	5.1%	<0.1%	5.1%
S3	25.2%	3.3%	<0.1%	3.3%
S4	24.4%	5.2%	<0.1%	5.15%

Emerging Organic Contaminants in Soil

All six soil samples contained detectable concentrations of EOCs with the number of compounds detected in each soil ranging from 1-3. Five of the twenty-five target EOCs were detected, including Androstenedione, EE2, mParaben, mTric and OPP. Of the five compounds detected mParaben was the most frequently detected in five of the six soil samples. Maximum concentrations detected ranged from 7.20 μg/kg for Androstenedione to 152.5 μg/kg for EE2. The results are presented in Table 3.13, including detection frequency, concentration ranges, along with a comparison to literature values. The maximum values detected in this study are greater than those previously reported in the literature especially for EE2. In this study the concentration range for EE2, ethinylestradiol ranged from 4.2-152.5 μg/kg these high concentrations were detected in samples S4 and S22. The maximum concentration of EE2 was detected where wastewater treatment plant effluent is irrigated to land. The lowest concentration of EE2 was detected where dairy farm effluent is irrigated to land. OPP was excluded from being displayed in the results due to unacceptable recoveries. The complete set of data is provided in the Appendix (Table 8.3).

Table 3.13: Data summary of analytes detected in soil samples with comparison to international concentrations detected in soil (n=6)

Analyte	Frequency	Range (μg/kg) dry weight	Literature range (μg/kg) dry weight	Reference
Androstenedione	2/6	0.8-7.2	0.07-1.4	[139]
EE2	2/6	4.2-152.5	0.3-1.2	[140]
mParaben	5/6	1.1-31.8	1.2-8.0	[141]
mTric	3/6	2.1-14.2	NT	-

NT= not tested for in the literature

OPP excluded from results due to unacceptable recoveries

3.3.3 Effluent

In situ physicochemical parameters of effluent

The in-situ parameters including pH, dissolved oxygen (DO), temperature and conductivity were measured prior to collecting effluent samples (Table 3.14). The pH of the effluent samples ranged from 7.1-7.4, the dissolved oxygen ranged from 0.28mg/L to 6.14mg/L. The temperature ranged from 14.1°C to 19.1°C and the conductivity from 398μScm^{-1} to 977μScm^{-1}**.**

Total Suspended Sediment

The TSS ranged greatly from 16.75 mg/L to 446.6 mg/L this is expected due to samples being collected from different sites and with varying degrees of treatment (Table 3.14).

Table 3.14: In situ parameters measured before collection of effluent samples and TSS measured in laboratory.

Site	Effluent type	Area	pH	DO (mg/L)	Temp (°C)	Conductivity (μScm^{-1})	TSS (mg/L)
WW1	WWTP	Amberley	7.4	1.29	17	639	49.3
WW2	WWTP	Ashburton	7.0	2.58	14.1	398	446.6
WW3	WWTP	Akaroa	NT	NT	NT	NT	16.8
DS1	Dairy shed	Lincoln	7.1	6.14	18.3	977	154
DS2	Dairy shed	Oxford	7.2	0.28	19.1	457	NT*

NT= Not tested, sample WW3 was collected by the Christchurch City Council

NT*=Not tested due to the great amount of organic matter, TSS was unable to be accurately determine.

Dissolved Organic Carbon in Effluent

The dissolved organic carbon in effluent was determined following the method in section 2.6 for all samples except DS2. Sample DS2 was analysed as a solid sample. The dissolved organic carbon ranged greatly from 17.5-190.3 ppm.

Table 3.15: Total carbon, total inorganic carbon and total organic carbon of effluent samples.

Site	DC (PPM)	DIC (PPM)	DOC (PPM)
WW1	24.1	2.5	21.6
WW2	20.1	2.6	17.5
WW3	45.4	27.4	18.0
DS1	190.6	0.28	190.3
DS2 *	8.0%	0.2%	7.8%

* Sample DS2 was unable to be analysed for dissolved organic carbon, therefore it was analysed for as a solid sample in the same way that soil was analysed for organic carbon.

DC = Dissolved carbon

DIC = Dissolved inorganic carbon

DOC = Dissolved organic carbon

Emerging Organic Contaminants in Effluent - Dissolved phase

The EOC detected most frequently in the dissolved phase of effluent samples was BPA, being detected in 3 of the 5 samples (Figure 3.3). There were no EOC detections in the dairy shed effluent sample DS2. The maximum concentrations detected in effluent ranged from 6.0 ng/L for BP1 to 811.8 ng/L for mParaben (Figure 3.4). Results for E1 and Androstenedione were excluded from the results due to unacceptable recoveries. The full data set is available in the Appendix (Table 8.4).

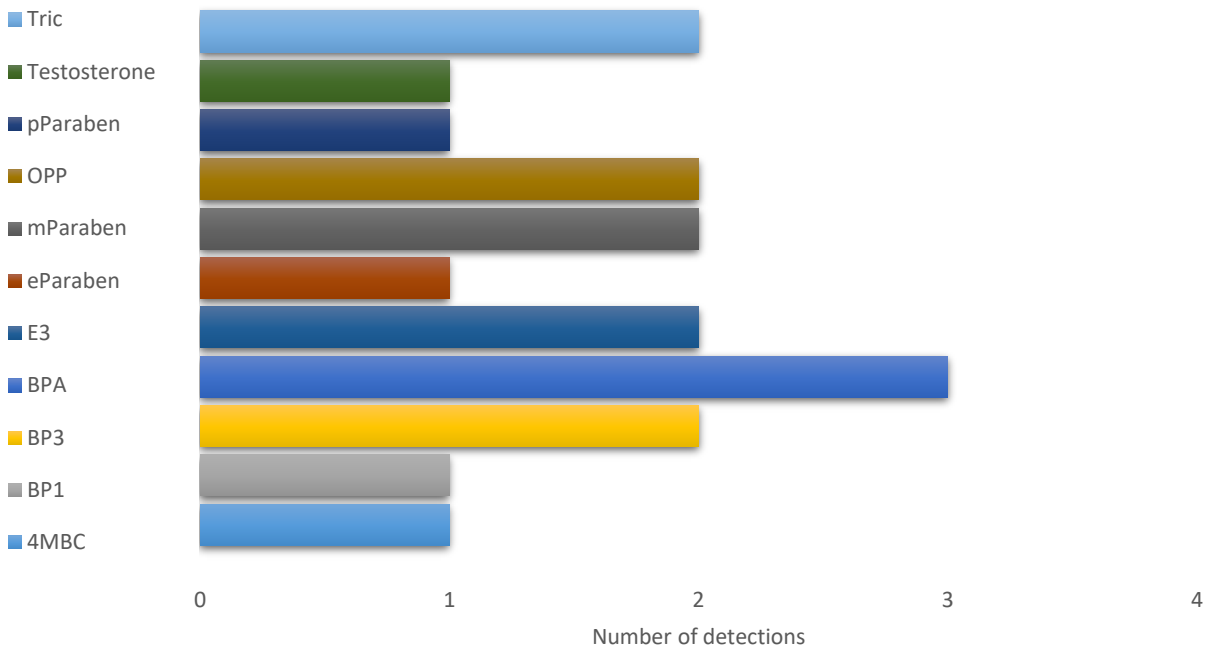


Figure 3.3: Analytes detected in dissolved phase of effluent.

Relationship between EOCs in Effluent and other parameters

There were no clear relationships for the number of EOCs detected and dissolved organic carbon or dissolved oxygen (Table 3.16).

Table 3.16: Comparing dissolved organic carbon and dissolved oxygen to the number of detections in effluent samples.

Site	DOC	DO	Number of EOC Detections		
			DP	PP	Total
WW1	21.6	1.29	1	2	3
WW2	17.5	2.58	7	5	12
WW3	18.0	NT	6	4	10
DS1	190.3	6.14	3	2	5

DP= dissolved phase PP=particulate phase

DOC= dissolved organic carbon DO= dissolved oxygen

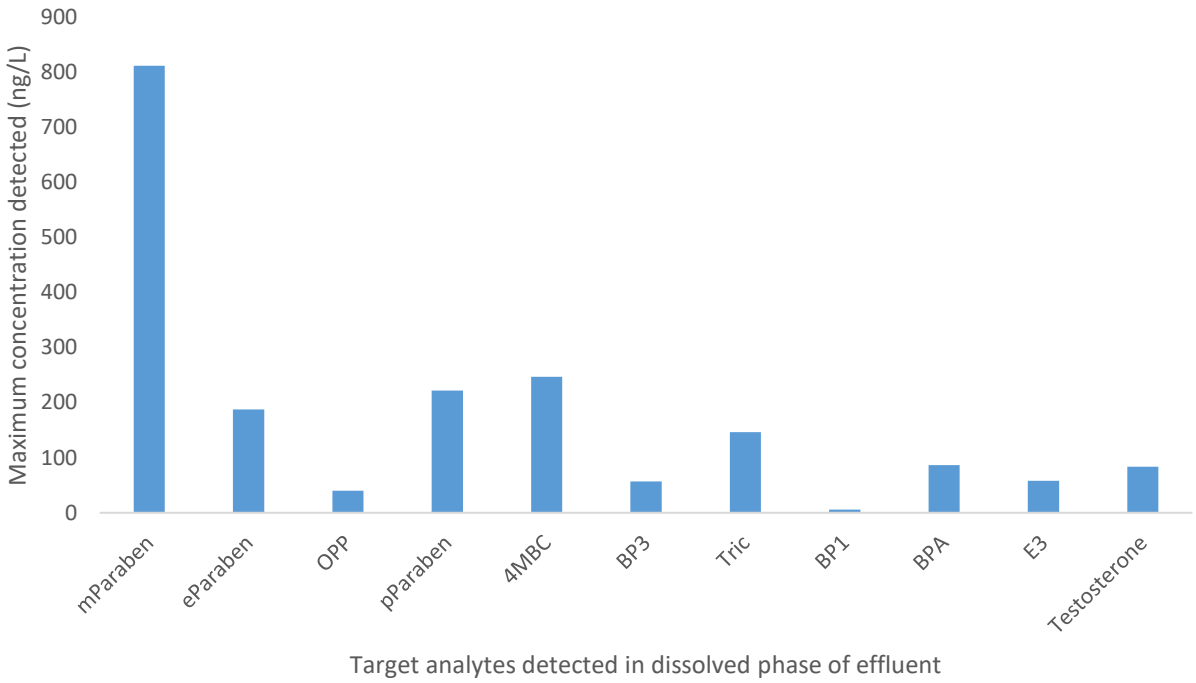


Figure 3.4: Maximum concentration of target analytes detected in the dissolved phase of effluent samples

Comparison of EOCs in effluent to literature values

Concentrations of EOCs detected in the dissolved phase were compared to international concentrations detected in influent and effluent samples (Table 3.17). Because the five effluent samples in this study are from various sites with varying degrees of treatment a better comparison is made with international concentrations for both influent and effluent. The concentrations for OPP, 4MBC, BP3, Tric, BP1, BPA, E3 and Testosterone detected in the effluent samples are comparable to effluent concentrations detected overseas. The relatively higher concentrations of mParaben, eParaben and pParaben are more comparable to international influent values. Higher concentrations of parabens were all detected in sample WW2 which was sampled prior to any treatment.

Table 3.17: Analytes detected in the dissolved phase of effluent samples showing the range of concentration detected with comparison to the literature values.

Analytes	Range of conc. Detected in this study (ng/L)	Literature values (ng/L)	Reference
BPA	11.0-86.8	In: 80-4980	[54]
		Eff: 6-3642	[54]
BP-1	6.0	In: 31-700	[142], [143], [144]
		Eff: <2-41	[142], [143], [145]
BP-3	42.5-56.7	In: 11-7800	[65], [143], [144]
		Eff: 3-2196	[142], [146], [65]
eParaben	187.7	In: 2.2-719	[147], [148]
		Eff: <0.3-69	[147], [142], [149]
E3	5.5	In: 10-660	[150]
		Eff: 0.4-151	[150]
4MBC	246.8	In: 278-6500	[146, 151]
		Eff: 42-2300	[65], [148]
OPP	8.9-40.0	In:	*
		Eff:	*
pParaben	222.0	In: 43-2640	[147], [152], [153]
		Eff: <0.25-95	[147], [142], [154]
Testosterone	83.7	In: 7.9-1261	[150]
		Eff:<0.3-20	[150]
Tric	89.0-146.3	In: 52-86200	[89]
		Eff: 10-5370	[89]

* = Data not available in the literature

Comparison of EOCs in effluent to literature values, continued

There are no overseas studies known to the author which analyse for EOCs in the particulate phase of effluent. One previous investigation of EOCs in WWTP influent and effluent in New Zealand analysed both the dissolved phase and particulate phase, [155] this is unique for both sets of data to be analysed. The dissolved phase is the sample following filtration and the particulate phase is the material present on the filter paper which is usually discarded. A comparison was made between the present study and the investigation of Gisborne WWTP (Table 3.18). The comparison was made between concentrations at different stages of treatment (pre-milliscreen, before biological trickling filter (BTF) and post BTF, the tabulated results from the Gisborne study are averaged for four samples collected over four weeks during October and November. Compounds detected in the dissolved phase of effluent in the present study were BP-3, eParaben, pParaben and testosterone and compounds detected in the particulate phase were BP1, chlorophene, OMC, 17α Estradiol and BP1. All compounds detected in the present study were present at similar concentrations to the Gisborne study, excluding BP-3 and OMC which were not analysed for in the Gisborne study. Compounds detected in both the dissolved and particulate phase were BPA, E3, mParaben, tric and 4MBC, all were detected at similar concentrations to the Gisborne study except 4MBC which was not included in the Gisborne study and E3 which was not detected in the particulate phase of the Gisborne study.

Table 3.18: Concentrations of target analytes detected effluent of this study compared to concentrations detected from a study of Gisborne WWTP

	This Study			Gisborne Study					
Analytes	Concentration dissolved phase	Concentration particulate phase		Pre-milliscreen n=4		Before BTF n=4		Post BTF n=4	
	(ng/L)	(ng/l)	(µg/Kg)	Diss. (ng/L)	Part. (µg/Kg)	Diss. (ng/L)	Part. (µg/Kg)	Diss. (ng/L)	Part (µg/Kg)
Androstenedione	**1.81-6.07**	-	**-**	75.8	7.84	55.8	8.72	**4.54**	4.99
BPA	**11.0-86.8**	1.7	**103.1**	341	-	**90.3**	-	4.9	**99.6**
BP-1	-	0.8-1.5	**30.4-46.4**	130	12.6	109	98.8	44.7	**37.3**
BP-3	42.5-56.7	-	-	NI	NI	NI	NI	NI	NI
Chlorophene	-	47.2	**26.4**	21.4	65.1	29.0	96	10.0	**27.5**
eParaben	**187.7**	-	-	**205**	266	**219**	41.8	-	-
E3	**5.52-58.3**	30.4	197.3	213	-	**143**	-	**19.1**	-
17α Estradiol	-	8.4	**54.7**	79.2	1519	73.9	1334	0.73	**19.0**
4MBC	246.8	38.3	21.4	NI	NI	NI	NI	NI	NI
mParaben	**48.4-811.8**	3.1	1.7	1881	204	**1389**	163	2.95	288
OMC	-	2.7-459.9	54.5-979.8	NI	NI	NI	NI	NI	NI
pParaben	**219.3**	-	-	667	66.3	**547**	21.4	1.85	-
Testosterone	**83.7**	-	-	**50.8**	2.9	34.5	-	0.12	1.1
Tric	**89.0-146.3**	27.9-334.9	**187.5-1667.6**	**93.5**	6183	**91.5**	**2495**	49.3	**294**

BTF= biological trickling filter

-= Not detected

NI = Not included in the Gisborne analysis

The Canterbury values highlighted in **bold** are relative to those **underlined** in the Gisborne study.

Distribution of analytes between the dissolved phase and particulate phase

For the majority of compounds detected in effluent, the concentration contributed from the dissolved phase was greater than that of the particulate phase, exceptions to this included chlorophene, OMC and 17α Estradiol which were not detected in the dissolved phase (Table 3.19). Triclosan was also detected at a greater concentration in the particulate than the dissolved phase for sample WW2.

Table 3.19: Concentrations of target analytes detected in the total effluent samples, there were no detections in sample DS2

	WW1			**WW2**			**WW3**			**DS1**		
Analytes	DP (ng/L)	PP (ng/L)	Total (ng/L)	DP (ng/L)	PP (ng/L)	Total (ng/L)	DP (ng/L)	PP (ng/L)	Total (ng/L)	DP (ng/L)	PP (ng/L)	Total (ng/L)
Androstenedione	6.07	-	**6.07**	-	-	-	1.81	-	**1.81**	-	-	**-**
BPA	-	-	**-**	11.0	-	**11.0**	16.4	1.7	**18.1**	86.8	-	**86.8**
BP-1	-	1.50	**1.50**	-	-	**-**	-	0.8	**0.8**	-	-	**-**
BP3	-	-	**-**	56.7	-	**56.7**	42.5	-	**42.5**	-	-	**-**
Chlorophene	-	-	**-**	-	47.2	**47.2**	-	-	**-**	-	-	**-**
eParaben	-	-	**-**	187.7	-	**187.7**	-		**-**	-	-	**-**
E3	-	-	**-**	58.3	-	**58.3**	5.52	-	**5.52**	-	30.4	**30.4**
mParaben	-	-	**-**	811.8	3.11	**814.9**	-	-	**-**	48.4	-	**48.4**
OMC	-	2.69	**2.69**	-	459.9	**459.9**	-	16.4	**16.4**	-	-	**-**
pParaben	-	-	**-**	219.3	-	**219.3**	-	-	**-**	-	-	**-**
Testosterone	-	-	**-**	-	-	**-**	-	-	**-**	83.7	-	**83.7**
Tric	-	-	**-**	146.3	334.9	**481.2**	89.0	27.9	**116.9**	-	-	**-**
4MBC	-	-	**-**	-	38.3	**38.3**	246.8	-	**246.8**	-	-	**-**
17a Estradiol	-	-	**-**	-	-	-	-	-	-	-	8.4	**8.4**

DP=dissolved phase

PP= particulate phase

Total concentrations are illustrated in **bold**

The K_d (solid-water partition coefficient) values were calculated for BPA, mParaben and triclosan as these compounds were detected in both the dissolved phase and particulate phase of a single effluent sample. The K_d is defined as the ratio of contaminant concentration in the solid fraction (Cs, µg Kg^{-1}) to the contaminant concentration in the aqueous phase (Cw, µg L^{-1}) [156]. It was not possible to calculate a K_d value for all compounds as some compounds were not detected either in the particulate phase or in the dissolved phase (Table 3.20). Values calculated for both BPA and triclosan were 3.8 and 3.1-4.3 respectively, similar to the literature K_d values of 2.1-3.1 and 3.7. There were no literature k_d values available for comparison with methylparaben.

Table 3.20: K_d values from effluent samples in this study compared to the literature, along with the number of detections in each phase

Analytes	Log K_d	Log K_d Literature	Reference	No. of detections in dissolved phase	No. of detections in particulate phase
BPA	3.8	2.1-3.1	[157]	3	1
BP-1	ND			0	2
BP-3	ND			2	0
Chlorophene	ND			0	1
eParaben	ND			1	0
E3	ND			2	1
17α Estradiol	ND			0	1
4MBC	ND			1	1
mParaben	0.3	*		2	1
OMC	ND			0	3
pParaben	ND			1	0
Testosterone	ND			1	0
Tric	3.1-4.3	3.7	[158]	2	2

ND = Not detected in both phases for one sample * = No K_d literature values available for comparison

Industrial Compounds

Bisphenol A was detected primarily in the dissolved phase of effluent samples in this study and was only detected once in the particulate phase, this finding contrasts with Comtois-Marotte et al (2017) who found bisphenol A to have the highest concentration in the particulate phase from 31 emerging contaminants of wastewater samples with an average concentration of 6230 ng g^{-1} [156].

Preservatives and Anti-Microbial Compounds

Methyl paraben was detected in both phases of effluent in this study. mParaben has a $LogK_{ow}$ of 2.09 and would be expected to exist in the dissolved phase. However previous studies have reported Methyl paraben in the particulate and sludge phase of sewage from the United States, Japan and Korea [159]. Chlorophene was only detected once in the particulate phase of effluent in this study, however, has been reported in sewage sludge and the dissolved phase of both WWTP effluent and rivers in overseas studies [160]. Ethyl paraben was also only present in the dissolved phase of effluent in this study, but has also been detected in sediment and sewage sludge in overseas studies [159]. Propyl paraben only existed in the dissolved phase of effluent samples in the present study nevertheless pParaben has also been detected in solid samples in the literature, including, agricultural soils and sediment [161]. Triclosan was detected in both phases of the present studies and has also been detected in both phases of the literature [115].

UV-filters

The UV-filter Benzophenone-1 was present only in the particulate phase of effluent in the current study, yet in a previous study by Emnet (2013), BP-1 was detected frequently in the dissolved phase of WWTP effluent, his study also detected BP-1 in marine sediments but not in the dissolved phase of seawater [115]. Benzophenone-3 was only detected in the dissolved phase of effluent in the current study, BP-3 can degrade to BP-1 by loss of a methoxy functional group [162], there could be some conversion occurring between BP-3 and BP-1. This could explain why BP-1 is not present in the dissolved phase. Octyl methoxycinnamate, a uv-filter was only detected in the particulate phase of effluent samples of this study however has also been detected in the

dissolved phase of seawater and surface water samples in the U.S.A. [163]. The uv-filter 4-MBC was detected in both phases of effluent in this study and has also been detected in both phases in the literature [164] [115].

Steroid Hormones

Estriol (E3) is predominantly thought to bind to the particulate phase in the environment due to its Log K_{ow} of 2.9 however, E3 was detected in both phases of effluent in the current study, and has also been detected in both the dissolved phase and sediment phase of two lakes in China [165]. Testosterone was also only detected in the dissolved phase of effluent in this study however, was detected in both the sludge and influent in a study undertaken in China [166]. The hormone 17α Estradiol was only detected in the particulate phase of effluent in the current study but has been detected in both phases of effluent in Gisborne [155].

3.4 Conclusions

EOCs were detected in all six soil samples and in four out of the five effluent samples. The number of compounds detected in each soil sample ranged from 1-3, five of the twenty-five target EOCs were detected in soil with mParaben being the most frequently detected in five of the six soil samples. Ethinylestradiol (EE2) was detected at particularly high concentrations compared to the overseas literature values. The other compounds detected in soil included mParaben and Androstenedione which were detected at concentrations similar to the literature, methyl triclosan was also detected, however, there was no literature available for comparison.

The target analyte detected most frequently in the dissolved phase of effluent was BPA, detected in 3 of the 5 effluent samples. Other compounds detected in the dissolved phase included mParaben, eParaben, OPP, pParaben, 4MBC, BP3, Tric, BP1, BPA, E3 and Testosterone. Concentrations detected in the dissolved phase were compared to international concentrations, the concentration detected in this study were comparable to effluent concentrations overseas except the three parabens mParaben, eParaben and pParaben which were comparable with international influent values.

Due to a lack of studies considering the particulate phase, the data from this study was compared to the only known study analysing both the dissolved and particulate phase, a study in Gisborne, New Zealand. The concentrations in this study were mostly of a similar magnitude to those analysed in the Gisborne study yet estriol (E3) was detected in the particulate phase in this study but was only detected in the dissolved phase of the Gisborne study, this is likely due to different effluent treatment processes. It is difficult to make comparisons between the particulate phase of effluent due to the lack of studies including analysis of this phase, more work is required in this area. This study will help contribute to the data which is lacking regarding the particulate phase of effluent.

The distribution of analytes between the dissolved phase and particulate phase was further investigated by calculation of K_d values (solid-water partition coefficients). Calculations of K_d values were only possible for BPA, triclosan and mParaben since most compounds were not detected in both phases of a single sample. Limited K_d values were available in the literature but were comparable for the values obtained for BPA and triclosan in this study. The literature was further assessed to see if there was similarity between compounds only detected in the solid phase or water phase of this study. The literature presented an overall absence of studies investigating the particulate phase. All of the compounds detected in either phase of effluent was detected in both phases in the environment, whether that be in soil, sludge, marine sediment, effluent, rivers or the marine environment. It is recommended that laboratory studies are undertaken under controlled conditions to determine the solid-water partitioning of EOCs.

CHAPTER FOUR

SURVEY OF EMERGING

CONTAMINANTS IN SHALLOW GROUNDWATER

CANTERBURY

4 Survey of Emerging Contaminants in Shallow Canterbury Groundwater

4.1 Introduction

The presence of EOCs in groundwater has faced increasing attention in overseas countries. Studies have been carried out in a variety of countries across Europe , the Middle East, North America and Asia [19]. Groundwater is an important resource, often used as a source of untreated drinking water, stock water and irrigation. It is therefore important that the environmental risks of EOCs in groundwater are properly evaluated.

There is a lack of investigation concerning groundwater contamination by EOCs in New Zealand. Previous research regarding EOCs in New Zealand has investigated their presence in the marine environment [115] streams and sediment [114] and wastewater influent and effluent [115]. Internationally the main sources of contamination have been identified to be landfills, animal waste, domestic waste, hospital waste and industrial effluent [19]. As these sources are present in New Zealand and New Zealand has similar use of compounds such as personal care products and industrial compounds, it is also likely for them to occur in groundwater at similar concentrations as overseas.

To date investigations overseas have focused on contamination only in the dissolved phase of groundwater and have omitted analysis of the particulate phase remaining on the filter paper once filtered.

This study is the first to investigate the presence of EOCs in groundwater in Canterbury, New Zealand and includes the analysis of both the dissolved and suspended phase. It was designed to be a preliminary study to determine if further research into EOCs in groundwater is warranted and if EOCs should be included into existing groundwater monitoring programmes.

4.1.1 Objectives

The specific objectives of Chapter Four were to:

- Determine if EOCs are present in the dissolved phase and suspended particulate phase of shallow groundwater wells (<25m depth) across the Canterbury region.
- Determine if there is any seasonal variation in EOC concentrations.
- Determine whether any correlations can be made between well depth, water quality parameters such as dissolved oxygen and organic carbon and the presence of EOCs.

4.2 Methods

4.2.1 Materials and Methods

The materials and experimental methods used to extract, prepare and analyse the groundwater is described in Chapter 2, Methods.

4.2.2 Sampling Locations

Eighteen sampling locations were selected based upon expert advice. Details for each location including location, depth, land use, and soil type are summarised in Table 4.1. This information was identified using Environment Canterbury (ECan) well cards and the ECan mapping database publicly available online. Wells were selected in areas thought to likely be contaminated by the target compounds. Groundwater samples were taken twice to account for seasonal variation. In Canterbury recharge of groundwater primarily occurs during winter from June to August when precipitation is highest [167]. The first round of sampling (spring) took place between June and September and the second round of sampling (summer) took place between October and December. The approximate location of the wells sampled is given to show the spread of the study (Figure 4.1). Groundwater wells were assigned a number to maintain anonymity of the well owner and precise location. Human ethics approval was applied for, but it was determined by the University of Canterbury Human Ethics Committee that it was not required.

The following criteria were used to select wells:

- Less than 25 metres deep
- Diameter of 50mm or greater to accommodate the submersible pump
- Permission from owner to sample groundwater wells

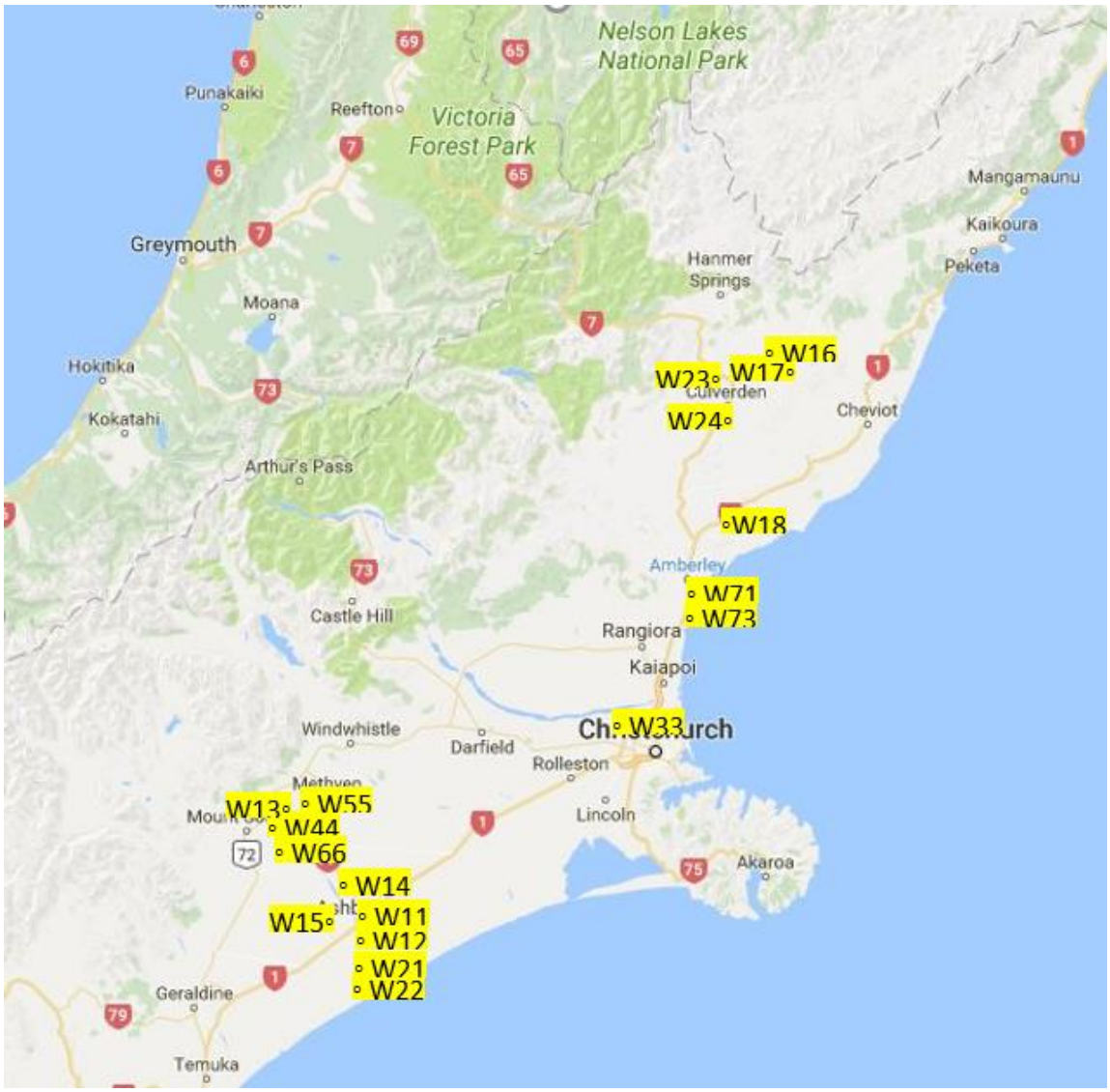


Figure 4.1: Map of Canterbury region showing approximation of each sampling well, with assigned numbers relevant to this study

Table 4.1: Summary of groundwater sampling locations and well details including depth, land use and soil type. Information was sourced from Environment Canterbury's online map database.

Well number	Location	Depth (m)	Land Use	Soil type
1) W71	Amberley	3.3	WWTP	Stony sandy loam
2) W73	Amberley	3.3	WWTP	Stony sandy loam
3) W11	Ashburton	7.2	WWTP	Clayey silt/ gravel
4) W12	Ashburton	8	WWTP	-
5) W21	Ashburton	7	WWTP	-
6) W22	Ashburton	12	WWTP	-
7) W33	Christchurch	22.2	Residential	Grey/Brown gravel
8) W55	Ashburton	3	Agricultural, dairy and pine plantation	-
9) W66	Ashburton	4	Agricultural, grazing dairy cows and other cattle	-
10) W44	Ashburton	6	Agricultural, beef dairy cows	-
11) W13	Ashburton	11.5	Agricultural	Deep silty loam
12) W14	Ashburton	10	Agricultural	Shallow silty loam
13) W15	Ashburton	9.75	Agricultural	-
14) W16	Hanmer Springs	7.30	Agricultural	-
15) W17	Waiau	6	Agricultural	-
16) W18	Omihi	9.1	Agricultural	-
17) W23	Culverden	9	Agricultural	-
18) W24	Culverden	5	Agricultural	-

- = Unknown soil type WWTP= Waste water treatment plant

4.2.3 Sampling Equipment

Sampling equipment was given special consideration to minimise contamination issues due to plasticizers being part of the target analytes. A submersible pump (Supertwister) paired with Teflon hosing was chosen as the most appropriate sampling apparatus. The pumps construction did contain plastic which does have some leaching potential however was the only appropriate pump for transportation requirements. This submersible pump required a 12V battery supply whereas the ideal pump (MP1) made from stainless steel required a large petrol generator. The teflon hosing was chosen after a previous round of sampling using garden hosing returned a high amount of contamination due to plasticizers.

4.2.4 Well Sampling Procedure

Prior to sampling, wells were purged three times the volume of the well as advised in the Ministry for the Environment protocol for groundwater sampling (Equation 6) [168]. To determine the purge time, at each well Equation 7 was used. This was necessary to ensure a representative sample of the groundwater was collected. Following purging of the wells, a bucket was filled with water to measure the in situ physicochemical parameters. A HACH HQ40d field multi meter was used to measure pH, conductivity and dissolved oxygen. The temperature was measured using the conductivity probe. Prior to each sampling day the pH and conductivity probes were calibrated using standard solutions.

Groundwater samples were collected from the teflon hosing attached to the submersible pump. One 4L sample was collected for the analysis of emerging contaminants and a 1L sample was collected for the analysis of total suspended sediment (TSS) and dissolved organic carbon (DOC). For each sampling trip field blanks were taken by exposing 4L of ultrapure Milli-Q water in an amber glass bottle with Teflon lined lid. A duplicate sample was also collected on each sampling trip. After sample collection, samples were returned to the laboratory on ice where the 4L samples were immediately acidified to a pH of 2. The samples were then stored in a fridge ready for analysis.

Equation 6: Purge volume (m^3) for groundwater wells

$$PV = 3\left(\frac{(\pi d^2\ h)}{4}\right)$$

PV= purge volume (m^3)

d = diameter of well casing (m)

h = height of water in well (m)

Equation 7: Purge time in seconds, calculated from the purge volume (m^3) and time taken to fill 8L bucket (sec).

$$PT = \left(\frac{PV}{8}\right)\ T$$

PT= purge time (sec)

PV= purge volume (L)

T= Time for 8L bucket to fill (sec)

4.3 Results and Discussion Groundwater

4.3.1 General Water Chemistry, TSS and DOC

General Water Chemistry

Over both sampling seasons, the pH ranged from 5.45-7.68. The average pH during the spring season was 6.43 (standard deviation of 0.46) and the average pH during the summer season was 6.52 (standard deviation of 0.64). The concentration of DO was variable ranging from 0.36 mg/L to 9.87 mg/L, and an average DO of 5.12 mg/L (standard deviation of 3.07 mg/L) over both sampling seasons. Low DO concentrations suggest longer residence time and isolation of the sample from the atmosphere [45] . The dissolved oxygen was relatively consistent between the first and second round of sampling except for well W16 which had a greatly decreased level of DO

during the second sampling round. The temperature over both seasons ranged from 7.8°C to 19.0°C. The average temperature over the spring season was 11.3°C (standard deviation 1.82°C) and the average temperature over the summer season was 13.4°C (standard deviation 2.73°C).The conductivity during the two seasons ranged from 37.9 μScm^{-1} – 570 μScm^{-1}, conductivity measures the concentration of dissolved solids in the sample, higher conductivity is indicative of groundwater which has had longer contact time with the minerals in the aquifer [45].

Table 4.2: In situ parameters measured at each groundwater well prior to sample collection

Well no.	**pH**		**DO (mg/L)**		**Temp (°C)**		**Conductivity (μScm^{-1})**	
Sampling round	1	2	1	2	1	2	1	2
W11	6.60	6.42	1.9	1.5	12.2	14.3	144.5	314
W12	6.60	6.60	1.9	1.5	13.8	19.0	286	403
W13	5.64	5.45	0.4	0.9	10.2	10.5	121	130.6
W14	5.95	5.8	9.3	7.7	10.9	11.4	366.3	316
W15	5.55	5.67	4.5	4.1	12.8	13.3	347.1	332.5
W16	5.94	6.1	4.5	0.8	10.0	11.4	446	128.7
W17	6.49	6.38	4.8	3.9	13.2	15.0	224.8	217.9
W18	6.55	6.33	4.2	3.2	11.2	12.3	575	524
W21	6.79	6.56	6.5	5.8	11.7	16.8	423	363
W22	6.62	6.46	4.3	4.3	12.2	18.5	570	455
W23	6.29	5.99	9.0	7.0	12.4	12.4	382.4	394.5
W24	6.52	6.34	4.5	6.0	12.4	14.4	274.6	273.2
W33	7.27	NT	9.6	NT	12.6	NT	97.6	NT
W55	6.5	7.02	8.5	8.5	9.0	10.5	105.3	112
W44	6.91	7.56	10.2	9.6	8.3	9.4	98.1	73.8
W66	6.6	7.68	9.9	7.4	7.5	11.8	37.9	52.4
W71	NT	7.17	NT	2.0	NT	12.7	NT	422
W73	NT	7.23	NT	1.2	NT	13.5	NT	728

1 = Sampling round 1, spring season

2 = Sampling round 2, summer season

Total Suspended Sediment

The TSS ranged greatly from 0 mg/L to 258.6 mg/L during the first round of sampling (spring season) and ranged from 0 mg/L to 127.4 mg/l during the second round of sampling (summer season). The reason for greater TSS during the spring season is thought to be due to greater rates of rainfall thus infiltration during this season.

Table 4.3: Total suspended sediment of 1L groundwater samples

Well no.	Total suspended sediment (spring season) (mg/L)	Total suspended sediment (summer season) (mg/L)
W11	258.6	11.3
W12	234.2	127.4
W13	1.3	0
W14	6.9	1.5
W15	1.7	2.7
W16	1	4.1
W17	0	0.1
W18	0	1.5
W21	133	13.4
W22	2.8	5.6
W23	3	6.2
W24	2.3	0.4
W33	0.1	NT
W55	0.2	0
W44	0	0.45
W66	0	0.05
W71	NT	1.7
W73	NT	11.9

NT= Not tested

Table 4.4: Total suspended sediment of 1L duplicate groundwater samples

Well no.	Total suspended sediment (spring season) (mg/L)	Total suspended sediment (summer Season) (mg/L)
W12 duplicate	170.1	114.4
W13 duplicate	0.8	NT
W15 duplicate	NT	3.5
W18 duplicate	0.4	NT
W24 duplicate	NT	0.4
W33 duplicate	0.2	NT
W44 duplicate	0.3	0
W71 duplicate	NT	1

NT= Not tested

Dissolved Organic Carbon in Groundwater

Over both sampling rounds the concentration of dissolved carbon (DC) ranged from 2.30 mg/L to 68.1 mg/L, the concentration of dissolved inorganic carbon (DIC) ranged from 1.98 mg/L to 52.5 mg/L. Dissolved organic carbon ranged from below the detection limit to 51.6 mg/L (Table 4.5). There was no significant difference in dissolved organic carbon between the two seasons.

Table 4.5: Dissolved Carbon, Inorganic and Organic Carbon of groundwater samples

Well:	Dissolved Carbon (mg/L)		Dissolved Inorganic Carbon (mg/L)		Dissolved Organic Carbon (mg/L)	
Sampling Round	**1**	**2**	**1**	**2**	**1**	**2**
W11	13.4	18.7	14.3	14.7	<0.05	4.0
W12	44.0	30.2	52.5	25.0	<0.05	5.2
W12 duplicate	56.9	31.7	29.4	21.9	27.5	9.8
W13	38.4	23.4	15.8	22.2	22.7	1.2
W13 duplicate	59.6	NT	16.4	NT	43.1	NT
W14	68.1	19.5	16.6	19.0	51.6	0.5
W15	36.8	19.5	12.2	18.5	24.5	1.0
W15 duplicate	NT	18.5	NT	16.9	NT	1.6
W16	11.7	11.6	7.9	10.3	3.8	1.3
W17	13	16.0	11.3	15.3	1.6	0.7
W18	33.9	33.1	27.1	28.6	6.8	4.5
W18 duplicate	33.7	NT	27.2	NT	6.5	NT
W21	19.4	22.5	18.4	18.7	1.1	3.8
W22	30.0	19.8	24.7	16.0	5.2	3.8
W23	17.1	16.2	13.4	15.	3.7	1.0
W24	17.6	20.1	15.7	18.4	2.0	1.7
W33	8.8	NT	8.2	NT	0.6	NT
W33 duplicate	8.7	NT	7.9	NT	0.8	NT
W44	6.2	6.4	7.6	5.9	<0.05	0.5
W44 duplicate	6.1	6.0	7.7	6.1	<0.05	<0.05
W55	7.4	11.4	8.2	9.5	<0.05	1.9
W66	2.3	2.5	2.0	3.2	0.3	<0.05
W71	NT	25.19	NT	16.5	NT	8.7
W71 duplicate	NT	27.0	NT	20.1	NT	6.8
W73*	NT	51.58	NT	48.87	NT	2.7

1 = Sampling round 1, spring season 2 = Sampling round 2, summer season
NT= Not tested

4.3.2 Emerging Organic Contaminants in Groundwater

During the first round of sampling, issues with the equipment meant data from W71 and W73 were excluded. During the second round of sampling W33 was unable to be included due to it being decommissioned. Particulate samples W11 and W18 from the second round of samples were unable to be included due to the tubes breaking during the extraction process.

Dissolved Phase

During this study, 13 of the 25 target EOCs analysed were detected in the dissolved phase of groundwater across both sampling seasons with maximum concentrations ranging from 0.461 ng/L for 3PBOH to 453.5 ng/L for OP (Table 4.6). The analyte OPP was detected in samples however was excluded from analysis in these results due to inadequate recoveries. Of the 33 wells sampled, 26/33 groundwater samples had at least one detection of a target analyte. The six wells in proximity to WWTPs had the greatest number of EOC detections, with detections in 100% of samples (Table 4.7). Whereas the wells used for public drinking water had the least number of EOC detections, with detections in 43% of samples.

Table 4.6: Detected target analytes in dissolved phase of groundwater samples across the Canterbury region

Analyte	Number of detections		Minimum concentration detected (ng/L)	Maximum concentration detected (ng/L)	Limit of detection (ng/L)	Literature concentration range (ng/L)	References
	spring	summer					
BPA	8	9	0.26	97.2	0.026	930	[42]
bParaben	2	1	1.08	19.4	0.097	19-32	[49]
BP-1	0	1	1.43	1.43	0.042	19.4	[46]
BP3	4	1	0.41	4.82	0.086	4.36-34	[47]
Chlorophene	1	1	2.15	33.2	0.117	NT	
eParaben	2	0	5.45	19.5	0.042	64-86	[49]
E3	1	0	3.03	3.03	0.319	0.16	[42]
mParaben	3	6	0.65	71.3	0.021	36-459	[48-49]
OMC	0	1	0.97	0.97	0.205	NT	
OP	1	5	Below LOD	453.5	1.140	42-190	[42, 45]
pParaben	2	3	0.95	11.7	0.137	3-61.9	[48-49]

NT = Not tested for in literature studies

Table 4.7: Detection frequency of target analytes in dissolved phase of groundwater across both sampling rounds by use of water, land use or monitoring type

Well description	Number of wells	Number of samples	Number of samples with detections	Percentage of samples with detections	Number of detections	Maximum number of detections in one well
Public drinking well	4	7	3	43%	3	1
WWTP monitoring	6	10	10	100%	41	7
General monitoring/ domestic drinking	8	16	13	81%	24	4
All wells	18	33	26	79%	68	7

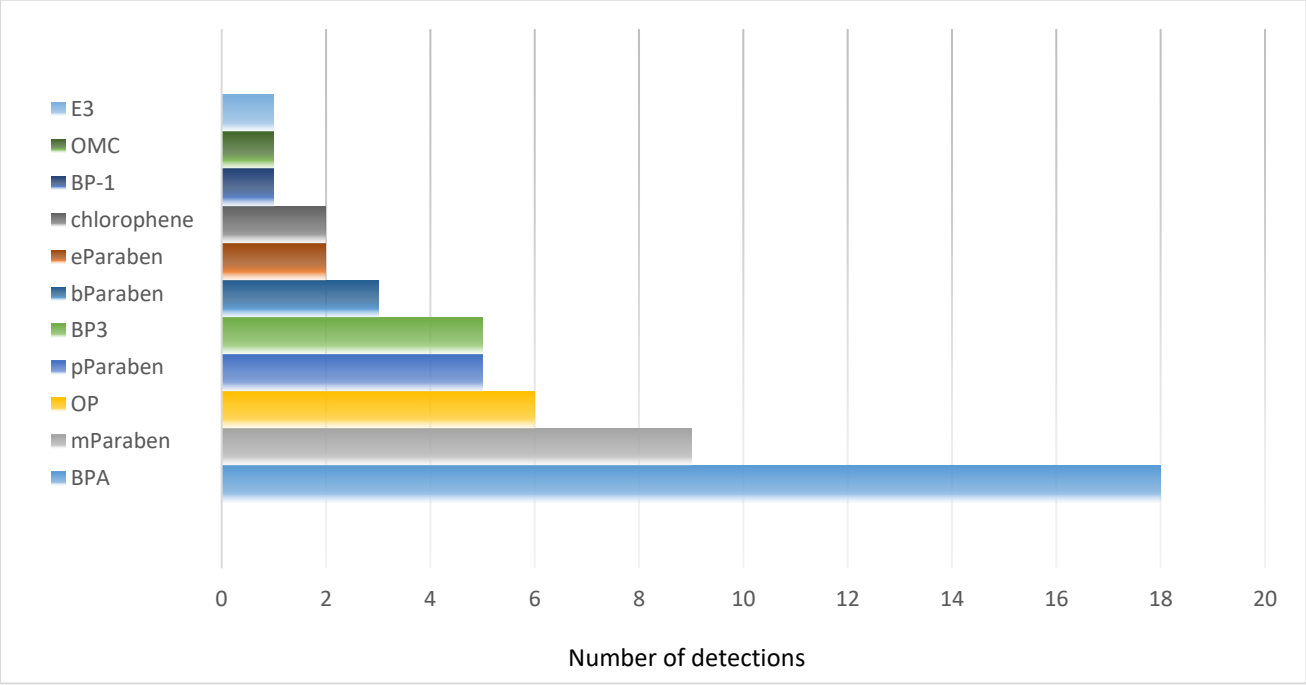


Figure 4.2: Number of detections of target analytes detected in dissolved phase of groundwater samples across both sampling rounds

Comparison of EOCs detected in dissolved phase of Canterbury groundwater to literature values

Concentrations of target analytes detected in this study were compared with concentrations detected in overseas studies (Table 4.6). Overall the concentrations detected in this study are generally comparable with the lower end concentrations detected internationally.

Preservatives

Methyl paraben was detected in 9 of the 33 wells sampled, 3 of these were in the spring sampling season and 6 were in the summer season. The concentrations detected ranged from 0.65-71.3 ng/L, these values are within the lower range of concentrations detected in the literature ranging from 36-459 ng/L (Table 4.6). Methyl paraben is detected relatively frequently in groundwater, it was detected in 2% of groundwater samples in UK groundwaters [169] and has been suggested as an indicator of waste water pollution [19]. Also, comparable with the low range concentrations in the literature was eParaben which was only detected during the spring season at concentrations ranging from 5.45-19.5 ng/L, these values were lower than those reported in the literature, with values reported ranging from 64-86 ng/L. Propyl paraben and butyl paraben were also detected at the lower end range of reported values, with propyl paraben ranging from 0.95-11.7 ng/L in this study and 3-61.9 ng/L in the literature. Butyl paraben ranged from 1.08-19.4 ng/L in Canterbury groundwater, comparable to the lower literature range of 19-32 ng/L. Chlorophene was detected twice, once during the spring season and once during the summer season at concentrations of 33.2 ng/L and 2.2 ng/L respectively, there were no reported values for chlorophene in the literature available for comparison.

Industrial Compounds

Bisphenol A (BPA) was the most frequently detected analyte in the dissolved phase of groundwater, being detected in 17 of the 33 samples. The concentration of BPA detected ranged from 0.26-97.2 ng/L which is at the lower end of concentrations reported in the international literature. Bisphenol A was also the most frequently detected EOC in overseas groundwater studies, detected in 100% of samples in both a Chinese study [76] and Germany [10]. Other EOCs detected in more than one sample were bParaben, BP3, chlorophene, eParaben, mParaben, OP,

and pParaben (Figure 4.2). OP an industrial compound, was detected once during the spring season and five times during the summer season at a concentration range below the LOD-453.5 ng/L, the majority of the detections of OP were within the ranges detected in the literature of 42-190 ng/L, it was only detected once at a significantly higher concentration of 453.5 ng/L during the spring season in well W12.

Ultra Violet filters

BP-3 and BP-1 are both uv-filters, and were detected 5/33 and 1/33 samples respectively at the lower end range of literature values of 0.41-4.82 ng/L and 1.43 ng/L (Table 4.6). Another uv-filter OMC was detected once in the dissolved phase of groundwater in this study at a concentration of 0.97 ng/L. There were no reported values in the literature available for comparison.

Steroid Hormones

The steroid hormone (E3) was detected once at a concentration of 3.03 ng/L this is significantly higher than that previously detected in the literature of 0.16 ng/L [42] .

Seasonal Analysis of EOC concentrations in dissolved phase

The number of target analyte detections for the dissolved phase were almost equal across both the spring and summer (Figure 4.3). There is no clear seasonal trend with 24 detections during the spring and 26 detections during summer. Both E3 and eParaben were only detected during spring. BPA was the most frequently detected compound during both sampling seasons. It was originally hypothesised that BPA was likely present due to the poly vinyl chloride (PVC) casings of the wells as also suggested in overseas studies investigating BPA in groundwater [170], further research is required to determine the source of BPA.

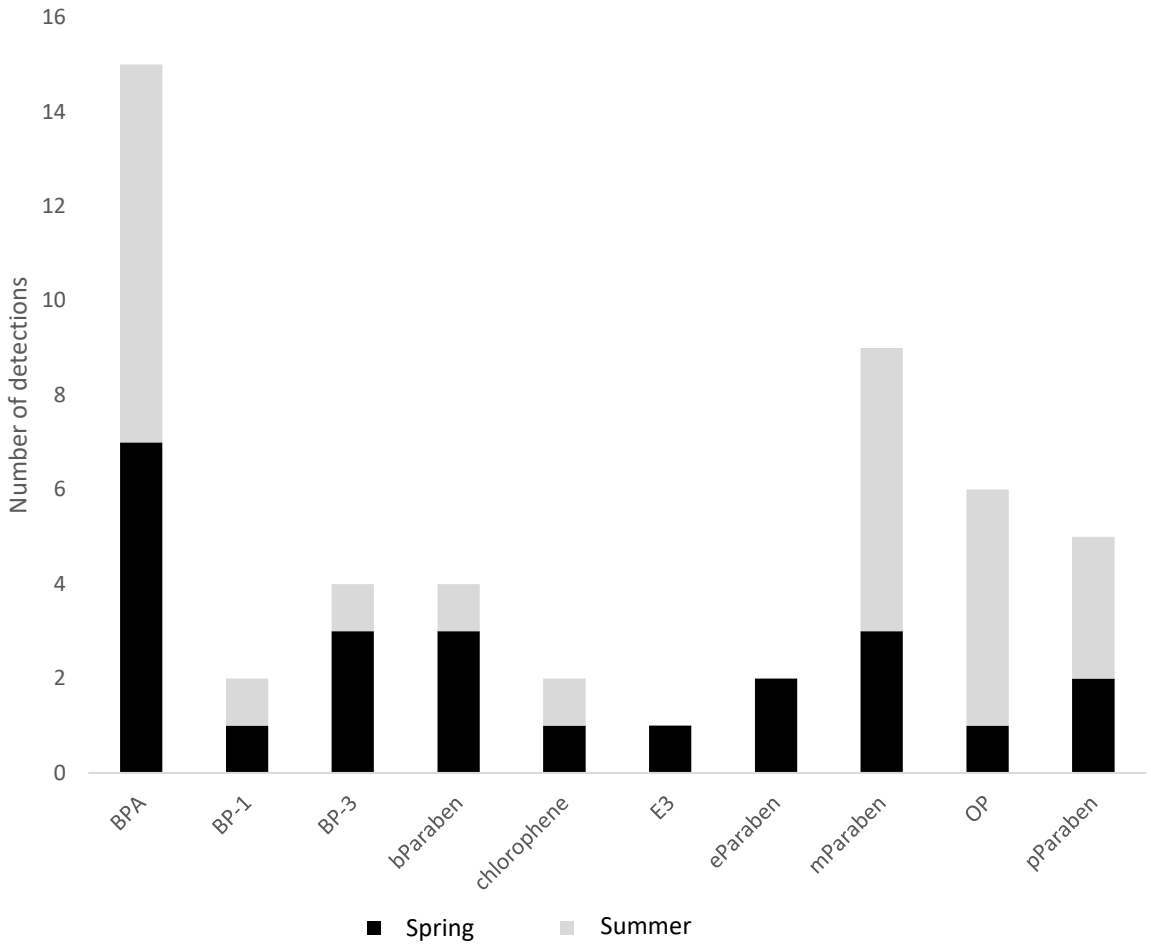


Figure 4.3: Number of detections of target analytes detected in dissolved phase of groundwater across both sampling rounds

Seasonal trends were further investigated for wells (W11, W12 and W21) as these wells had more than five target analyte detections during either sampling season (Figure 4.4). It is clearly seen that concentrations of target analytes were significantly greater during spring compared to summer, this is most likely due to recharge occurring during winter.

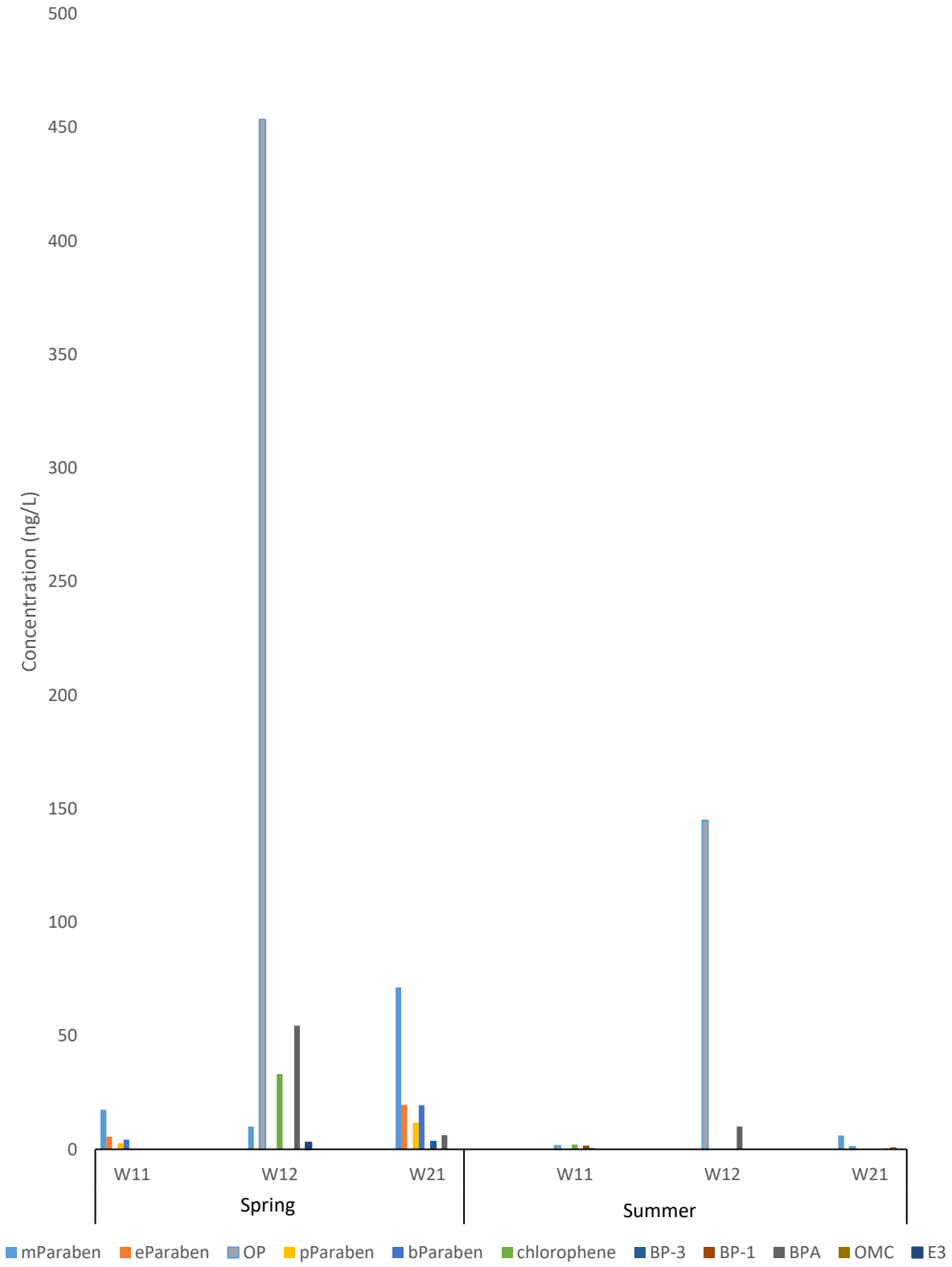


Figure 4.4: Wells (W11, W12, W21) which contained the greatest number of target analytes, comparison of concentrations during spring season and summer season

Particulate Phase Analysis for EOCs

Thirteen of the twenty-five target analytes were detected in the particulate phase during both sampling rounds including Androstenedione, BPA, BP1, BP3, chlorophene, E3, 4MBC, mParaben, mTric, OMC, OP, pParaben and Testosterone. There was at least one detection in 11/34 samples. Maximum concentrations ranged from 1.43 ng/L for E3 and testosterone to 22.3 ng/L for BPA. The most frequently detected compound in the particulate phase was BPA which was detected in 7/34 samples.

Particulate concentrations are presented in both ng/L and μg/Kg (Table 4.8). Some of the concentrations listed in μg/Kg are unexpectedly high. As noted for the dissolved phase of the groundwater samples, the six wells in proximity to WWTPs also had the greatest number of EOC detections in the particulate phase, with detections in 55% of samples. In general, compared to the dissolved phase, analytes were detected infrequently in the suspended phase.

Table 4.8: Detected target analytes and maximum concentration analysed in the particulate phase of groundwater samples from across the Canterbury region

Analyte	Number of detections	Maximum concentration detected particulate phase		Limit of detection (ng/L)
		ng/L	μg/kg	
Androstenedione	2	0.31	57.5	1.184
BPA	6	0.78	3907	0.030
BP1	3	1.93	4818	0.007
BP3	2	1.87	623	0.024
Chlorophene	1	1.67	555	0.017
E3	1	0.36	7.47	0.023
mParaben	5	9.96	829	0.016
4MBC	1	2.26	754	0.127
mTric	1	2.10	702	0.009
OMC	1	3.02	1005	0.093
pParaben	1	6.79	566	0.025
Testosterone	1	0.36	66.0	0.108

Seasonal analysis for EOCs in particulate phase

Most of the detections for the particulate phase were during spring rather than summer (Figure 4.5). The total suspended sediment was also greater during the spring season compared to the summer season therefore it is not unexpected that detections would be greater during the spring season. Two of the steroid hormones E3 and testosterone, were only detected during the summer season. There are no overseas studies known to the author which analyses the suspended particulate phase of groundwater samples, samples are generally filtered prior to extraction and the filter is discarded, more research is required in this area.

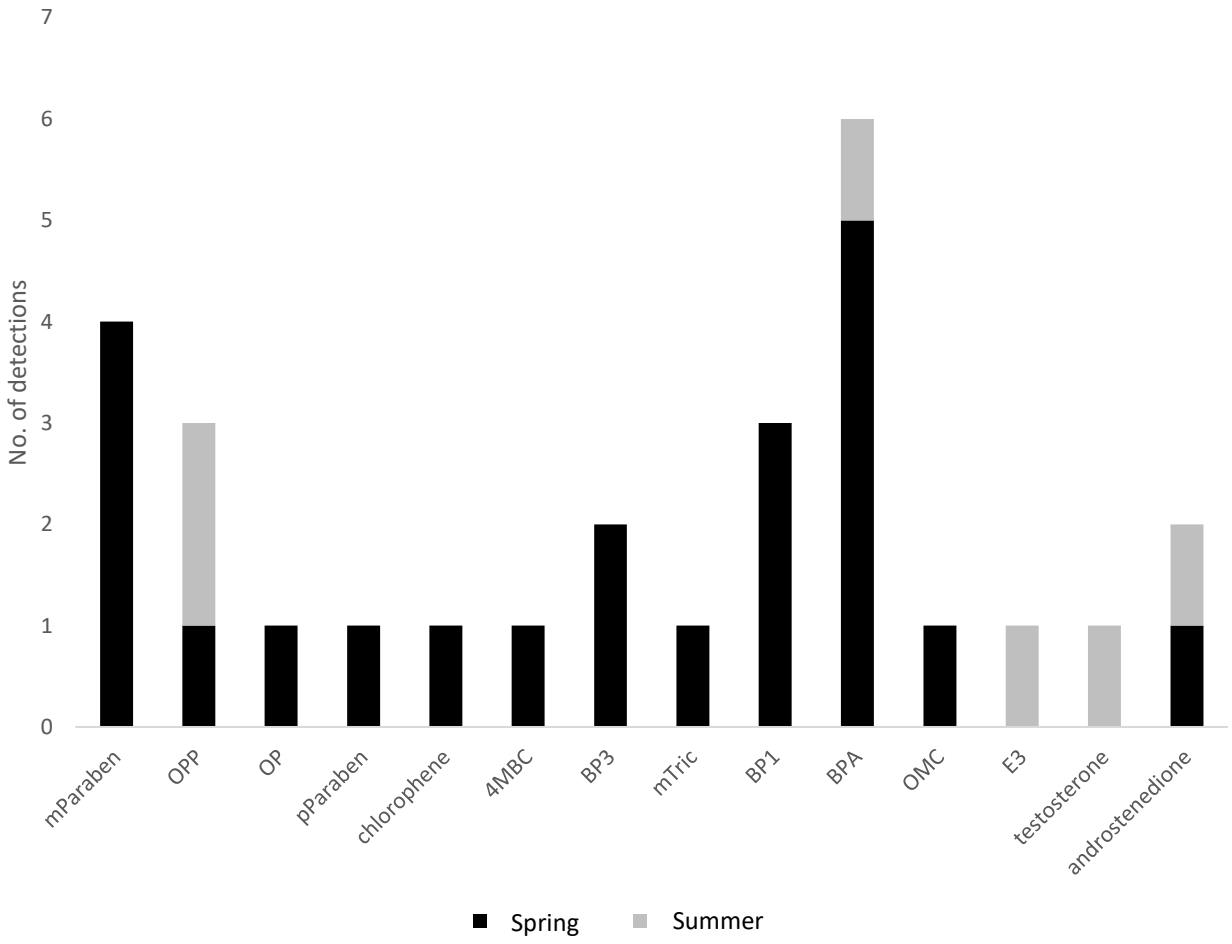


Figure 4.5: Number of detections of target analytes detected in particulate phase of groundwater across both sampling rounds.

Total Emerging Organics Contaminant Concentrations (dissolved phase + particulate phase)

The total EOC concentrations for each groundwater sample are displayed in the Appendix, Table 8.1 (first sampling round) and Table 8.2 (second sampling round). The maximum concentrations detected for each target analyte in each phase of groundwater are presented in Table 4.9. The majority of EOC concentrations are contributed by the dissolved phase. Androstenedione, 4MBC, mTric, OMC and testosterone were only detected in the particulate phase.

Table 4.9: Maximum concentrations of target analytes detected in each phase of groundwater samples

Analyte	Max. Conc. Dissolved Phase ng/L	Max. Conc. Particulate Phase ng/L	Max. Total Concentration ng/L
Androstenedione	ND	0.3	**0.3**
BPA	97.2	0.8	**98.0**
BP1	1.4	1.9	**3.36**
BP3	4.8	1.9	**6.69**
bParaben	19.4	ND	**19.4**
chlorophene	33.2	1.7	**34.87**
E3	3.0	0.4	**3.39**
eParaben	19.5	ND	**19.5**
4MBC	ND	2.3	**2.26**
mParaben	71.3	10.0	**81.3**
mTric	ND	2.1	**2.10**
OMC	ND	3.02	**3.02**
OP	453.5	ND	**453.5**
pParaben	11.7	6.79	**18.49**
Testosterone	ND	0.36	**0.36**

ND = Not detected

Distribution of analytes between dissolved phase and particulate phase

The distribution between the particulate phase and dissolved phase can provide useful insight into the processes controlling the transport of contaminants [171]. The solid-water distribution coefficients K_d (L Kg^{-1}) were calculated for analytes which were detected in both the dissolved phase and particulate phase of a single sample. Solid water distribution coefficients from the present study were 1.4-4.6 for BPA, 1.9 for BP3, and 1.9-2.4 for mParaben, where available they are compared to literature K_d values (Table 4.10). Limited K_d values were available in the literature. The K_d values for BPA and BP3 were comparable to the literature values available, having values of 4.4-8.5 and 2.3 respectively. The K_d values calculated in this study for BPA were similar for groundwater and effluent with values of 1.4-5.6 and 2.1-3.1 respectively. The K_d values for mParaben in this study however were significantly different for groundwater and effluent with values of 1.9-2.4 and 0.3 respectively. The K_d value for BP3 could only be calculated for groundwater therefore no comparison could be made with effluent.

Table 4.10: Solid-water distribution coefficient values for target analytes detected in both phases

Analyte	K_d (L Kg^{-1})	No. of detections dissolved	No of detections in particulate	Detections in both phases for single sample	Literature K_d values (L Kg^{-1})	Ref.
Androstenedione	-	0	2	0		
BPA	1.4-5.6	16	6	3	4.4-8.5	[167]
BP-1	-	2	3	0		
BP3	1.9	4	1	1	2.3	[172]
bParaben	-	4	0	0		
Chlorophene	-	2	1	0		
eParaben	-	2	0	0		
4MBC	-	1	1	0		
E3	-	1	1	0		
mParaben	1.9-2.4	9	5	2	*	
OMC	-	1	1	0		
OP	-	6	0	1		
pParaben	-	5	1	0		
Testosterone	-	0	1	0		

K_d = Solid water distribution coefficient *= No literature values available for comparison

The octanol water partitioning coefficient K_{ow} can be used to predict a compounds sorption to the particulate phase with compounds of log $K_{ow} > 4.0$ predicted to sorb to sediment. Compounds detected in each phase were compared to their Log K_{ow} values (Table 1.2). Both androstenedione and testosterone were detected only in the particulate phase, however both had log K_{ow} values less than 4.0. Methyl paraben was detected in both the dissolved phase and particulate phase yet its Log K_{ow} value of 2.09 which is suggestive of low sorption.

In this study K_{ow} was not a good predictor for the presence of a compound in the particulate phase. The findings from this study may be explained by a study by Fairbairn et al (2015) which found that K_{ow} values often failed to accurately predict distributions of less hydrophobic emerging organic compounds in sediment because the K_{ow} values do not account for non-hydrophobic interactions, these are interactions that can occur between amine, carboxylic and hydroxyl functional groups. Fairbairn et al (2015) found that for more hydrophobic compounds sediment–water distributions were generally well-predicted by K_{ow} [173]. It is also important to note that during the Canterbury study 1.2 μm filters were used therefore some colloidal material may be present in the dissolved fraction.

Total EOC concentrations and relationships with other parameters

Well Depth

The wells sampled were all less than 25 meters in depth, wells were grouped into sub groups to determine if there was a relationship between contamination and well depth (Table 4.11). The average total concentration (dissolved + particulate) was calculated for the five most commonly detected analytes for each well depth group, this was done for both seasons. The majority of detections during both seasons were in the wells of depth between 4-8 meters (Figure 4.6). These results are biased as they do not consider the use of the wells, as wells in the 4-8m category also contain the greatest percentage of WWTP monitoring wells. Further details regarding the surroundings of each well are listed in Appendix 2.

Table 4.11: Wells grouped in terms of well depth

Depth	Wells
≥4m depth	W55, W66, W71 and W73
Above 4m – 8m	W24, W21, W11, W16, W44, W22, W12 and W17
<8 m	W18, W23, W14, W13, W15 and W33

Well purpose:
public drinking water
waste water treatment plant monitoring wells
general monitoring and domestic drinking water

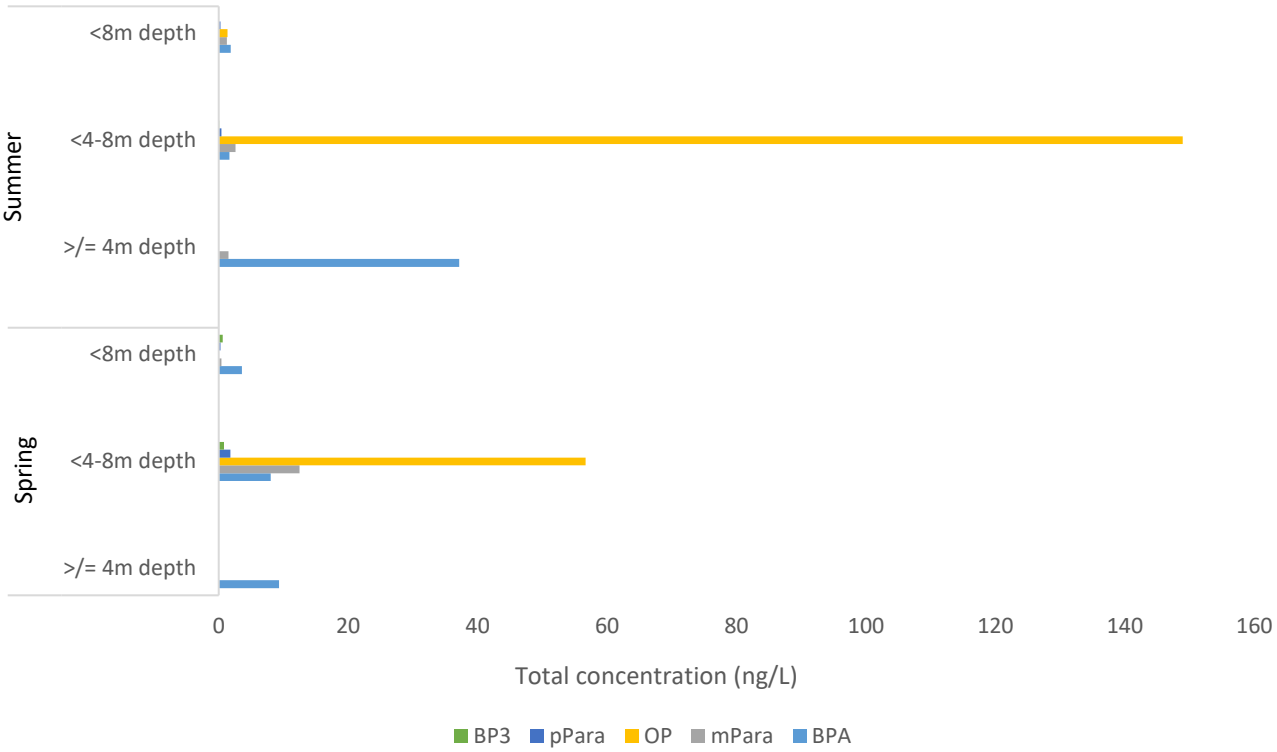


Figure 4.6: Average analyte concentration for the five most frequently detected analytes (total (ng/L) = dissolved ng/L + particulate (ng/L)

Dissolved Oxygen

Wells were grouped into three categories dependant on the concentration of dissolved oxygen measured in situ (0-2 mg/L absent to low DO, >2-6 mg/L low to medium levels of DO and 6-10 mg/L mid to high levels of DO). Categories were chosen based on the results detected in this study and are categorized in a similar way to a previous study analysing DO in Texas groundwater [174]. Wells with a DO $\geq$ 0.5 mg/L are considered oxic and wells with DO < 0.5 mg/L are considered anoxic [175]. Only one well W13 was measured as being anoxic during the first sampling round. The average number of detections were calculated from the number of detections in the dissolved and particulate phase (Table 4.12). The average number of detections for each group were 4.4 for 0-2 mg/L, 1.8 for >2-6mg/L and 2.9 for >6-10 mg/L. There was no clear relationship between the dissolved oxygen and average number of EOC detections (Table 4.12). However, there were

a greater total average number of EOC detections in the dissolved phase of wells for the lowest DO category (0-2 mg/L). There was also a relationship between the total number of detections in the dissolved phase and dissolved oxygen. The greatest number of target analytes were detected for the lowest category of DO and detections decreased with increasing DO. This negative correlation for DO and EOCs has also been reported in the literature for studies in soil and surface water [176] [177]. Higher DO has also shown increased removal for some EOCs in constructed wetlands [178]. Groundwater environments are typically low in DO [19]. Due to DO being necessary for lifeforms including microbes to exist, microbial degradation is significantly lowered in groundwater [19]. There appears to be no relationship between detections in the particulate phase and dissolved oxygen.

Table 4.12: Wells grouped in terms of dissolved oxygen with average number of EOC detections

DO (mg/L)	No of wells in category	Total No. EOC detections (dissolved)	Total No. EOC detections (particulate)	Average no EOC detections (Total)
0-2	9	28 (3.1)	12 (1.3)	4.4
>2-6	12	20 (1.7)	1 (0.08)	1.8
>6-10	12	18 (1.5)	17 (1.4)	2.9

Average detections for respective phases are displayed in (brackets)

Due to BPA being the most frequently detected target analyte, an analysis was carried out to see if there was a correlation between dissolved oxygen concentration and the presence of BPA (Figure 4.7). BPA was detected most frequently in wells with a DO between 0-2 mg/L. This result is expected due to low DO being an indicator for longer residence time and isolation from the atmosphere.

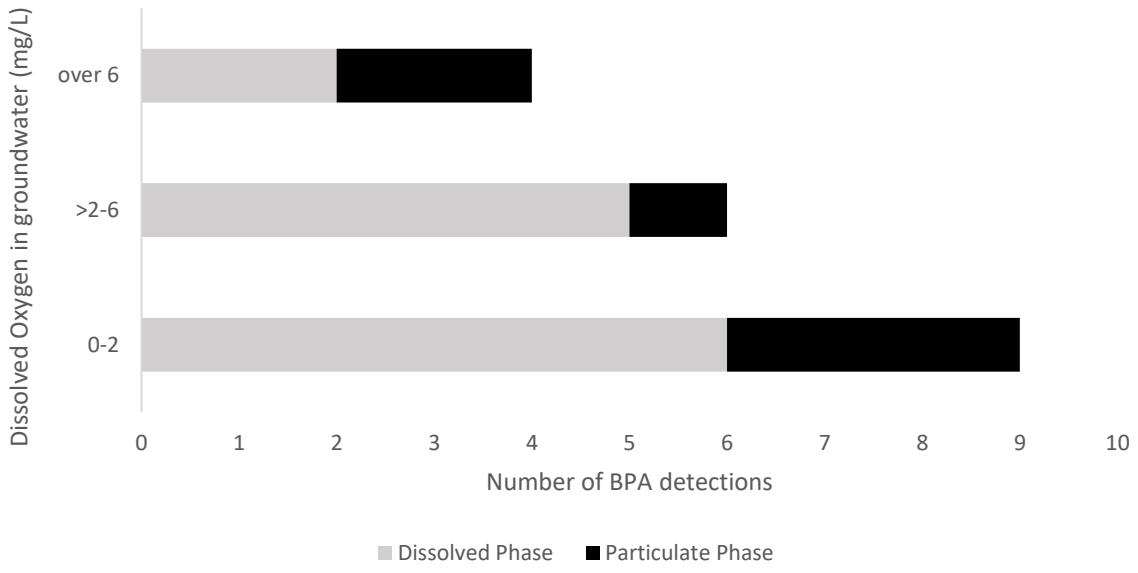


Figure 4.7: Number of BPA detections for relevant dissolved oxygen concentrations

Dissolved Organic Carbon

Wells were grouped into three categories dependant on the concentration of dissolved organic carbon detected (0-4 mg/L, <4-8 mg/L and 8 and above mg/L). Measured dissolved organic carbon concentrations from natural unpolluted groundwater are typically below 4 mg/L, concentrations above this level usually indicate anthropogenic influences or contamination issues [179]. The majority of wells (25/33) had concentrations of DOC below 4 mg/L (Table 4.13). The average number of detections were calculated from the number of detections in the dissolved and suspended particulate phase. The total average number of detections for each group was similar, with an average of 4.3 detections for 0-4 mg/L, 3.0 detections for <4-8 mg/L and 2.3 detections for 8 and above mg/L, the total average number of detections appeared to decrease with increasing DOC. There were also a far greater total number of detections for both phases for the 0-4 mg/L category of DOC, this result is conflicting with the statement found in the literature, where samples typically below 4 mg/L are indicative of a lack of anthropogenic contamination.

Table 4.13: Wells grouped in terms of dissolved organic carbon and compared with average number of EOC detections

DOC (mg/L)	No of wells in category	Total No. EOC detections (dissolved)	Total No. EOC detections (suspended)	Average no EOC detections
0-4	25	27 (1.1)	80 (3.2)	4.3
<4-8	5	4 (0.8)	11 (2.2)	3.0
8 and above	3	0 (0)	7 (2.3)	2.3

DOC= dissolved organic carbon

Average detections for respective phases are displayed in (brackets)

An analysis was carried out to see if there was a correlation between BPA and dissolved organic carbon (mg/L) (Table 4.14). There was no relationship between the dissolved organic carbon and percentage of samples with BPA, with the percentage of samples with BPA being similar 30-40% for all categories of DOC. The total number of BPA detections were greatest for the lowest DOC category; however, this result is most likely due to the high number of wells within this group.

Table 4.14: Correlation between dissolved organic carbon and BPA detections

DOC (mg/L)	No of wells in category	No. of BPA detections		Total BPA detections	Total possible detections	Percentage of samples with BPA
		dissolved	suspended			
0-4	25	11	4	15	50	30%
<4-8	5	4	1	5	10	40%
8 and above	3	2	0	2	6	33%

DOC= dissolved organic carbon

Groundwater Ubiquity Scores

Earlier in section 1.4, groundwater ubiquity scores were discussed as useful predictors of leachability and likelihood of a contaminant reaching groundwater. The scores earlier assigned were revisited to see whether there was a correlation between GUS and number of detections of an analyte in groundwater. The compounds detected during both rounds of groundwater sampling are listed in order from the highest number of detections to the lowest number of detections (Table 4.15). Interestingly BPA which was detected in 18/33 samples and is at the top of the list despite having an extremely low level of leaching potential along with OP which was detected in 6/33 samples and having a low leaching potential. However, if these two irregularities are excluded it is generally seen that the compounds with greater leaching potential (high/medium) were detected more frequently compared to those with low and extremely low leaching potential. It is difficult to make a solid conclusion from a small set of sampling data like this, further investigation is needed to exclude the potential for BPA and OP leaching from the well casing materials. Previous research has confirmed that BPA has the ability to leach from PVC material [180].

Table 4.15: Groundwater ubiquity scores compared to the number of detections in the dissolved phase of groundwater.

Compound	Concentration range (ng/L)	No. of detections	GUS	Leaching Potential to GW
BPA	0.3-97.2	18/33	-1.0	E. Low
mParaben	0.6-71.3	9/33	3.0	High
OP	1.1-453.5	6/33	0.002	Low
BP3	0.4-4.8	5/33	1.9	Moderate
pParaben	0.9-11.7	4/33	2.3	Moderate
bParaben	1.1-19.4	3/33	0.4	Low
eParaben	5.4-19.5	2/33	2.7	Moderate
Chlorophene	2.2-33.2	2/33	-0.5	E. Low
3PBOH	0.5	1/33	2.4	Moderate
BP1	1.4	1/33	1.4	Low
OMC	1.0	1/33	0.01	Low
E3	3.0	1/33	1.7	Low

GUS= Groundwater ubiquity score

GW= Groundwater

4.4 Conclusions

EOCs are present in Canterbury shallow groundwater. It is important to note that wells were selected on a worst-case scenario basis, where contamination was considered likely to occur. These results present only a snapshot in time and are relevant to the environmental conditions under which they were sampled, this study cannot be used as a general representation of New Zealand's groundwater. During both sampling seasons, 13 of the 25 EOCs analysed were detected in the dissolved phase of groundwater with maximum concentrations ranging from 0.461 ng/L for 3PBOH to 453.5 ng/L for OP. Of the 33 wells sampled 26/33 wells had at least one detection of a target analyte. Wells in proximity to WWTPs had the greatest EOC detections compared to public drinking water wells which had the fewest EOC detections. Bisphenol A (BPA) was the most frequently detected EOC across both sampling seasons. Overall the concentrations detected in the study were of similar magnitude but at the lower end of concentrations detected internationally. Two target analytes detected at slightly higher concentrations than international values were OP and E3 detected at 453.5 ng/L and 3.03 ng/L respectively.

There was a seasonal trend seen for the dissolved phase of groundwater for the three wells with the greatest number of EOC detections, with increased concentrations observed during the spring sampling season, most likely because this is when recharge occurs. There was also significant seasonal difference for the particulate phase of groundwater analysed, with most of the detections during the spring season. Thirteen of the 25 target compounds were detected in the particulate phase including mParaben, OP, pParaben, chlorophene, 4MBC, BP3, mTric, BP1, BPA, OMC, E3, Testosterone and Androstenedione.

The distribution of analytes between the dissolved phase and particulate phase was analysed by calculating K_d values for compounds detected in both phases of a single sample, this was only possible for BPA, BP3 and mParaben, values were comparable to literature K_d values. For further analysis compounds detected in each phase were compared with their log K_{ow} values, which are often used to predict the likelihood of a compounds sorption to sediment. Log K_{ow} values were not a good predictor for the presence of a compound in the particulate phase and this could be attributed to non-hydrophobic interactions which are not accounted for in K_{ow} values.

Correlations between EOC detections and various parameters were examined. A relationship was observed between groundwater depth and presence of EOCs, with greater detections in wells between 4-8m deep, this result is biased due to this category also containing the greatest percentage of WWTP monitoring wells. A relationship between dissolved oxygen and number of detections in the dissolved phase was also seen with the greatest number of EOCs detected in the dissolved phase for wells with DO between 0-2 mg/L, this was also seen for the number of BPA detections, which were also greatest when DO was between 0-2 mg/L. Overall there was a decrease in EOC detections in the dissolved phase with increasing DO. This result is consistent with low DO being indicative of a longer residence time. A relationship between dissolved organic carbon and EOC detections was also examined. The majority of wells measured DOC between 0-4 mg/L, DOC<4 is thought to be indicative of groundwater unaffected by anthropogenic activities yet the number of EOC detections was also greatest for this group of wells, the number of BPA detections were also conflicting to this, with the highest number of detections of BPA in wells with DOC ranging from 0-4mg/L.

Finally, the number of detections of target analytes in the dissolved phase were compared with the calculated groundwater ubiquity scores. Generally, the GUS calculated for each compound were good predictors of an analytes leachability to groundwater, however for two compounds BPA and OP the GUS results were inconsistent. More research is needed to confirm whether OP and BPA are leaching from the well casing material.

CHAPTER FIVE

RISK ASSESSMENT FOR

EOCS IN GROUNDWATER

5 Undertaking a Risk Assessment

5.1 Introduction

Due to the abundance of different chemicals released into the environment it is important to resolve which chemicals pose the greatest risk. This can ensure that monitoring programmes are more focused and therefore more cost effective.

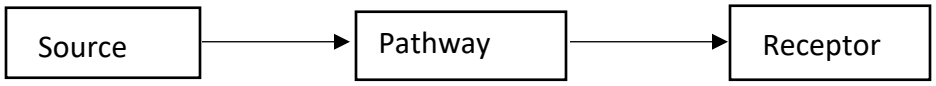
The purpose of this chapter is to obtain a better understanding of the potential impacts of EOCs in groundwater if any, and to identify priority contaminants based on emerging organic contaminants detected in the 18 groundwater wells sampled across the Canterbury region.

Ecological Risk Assessment Process

In New Zealand risk assessors generally follow the United States Environmental Protection Agency (US EPA) approach when undertaking an ecological risk assessment and therefore this process has been followed for this study. An ecological risk assessment as defined by the US Environmental Protection Agency is "a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors" (US EPA, 1998).

Ecological risk assessments follow a sequential order of steps:

1. The first step in an ecological risk assessment is **planning and scoping**. This step involves planning and research, who, what and where is at risk? What is the environmental hazard of concern? Where do these environmental hazards come from?
2. The second step involves **problem formulation**. The objective of this step is to identify what needs to be protected and what endpoints will be assessed. Once assessment endpoints are chosen, a conceptual model is developed of:



3. The third step involves **analysis**. This involves calculating the level of exposure of ecological receptors and identifying if the level of exposure is likely or not to cause harmful ecological effects. Calculations used may include hazard quotients to quantify risk and various parameters to determine the levels of exposure to a stressor.
4. The fourth step is **risk characterization**. The purpose of this phase is to use the results of analysis to estimate the risk that is posed on ecological entities and for the assessor to indicate the overall degree of confidence in the risk assessment by summarizing uncertainties, citing evidence to support the risk estimates and interpret the adverse ecological effects.

Objective

The purpose of this chapter was to perform a screening level risk assessment to decide whether EOCs detected in Canterbury shallow groundwater pose potential risk to the aquatic environment and human health. A screening level risk assessment as defined by the US EPA is, "a simplified risk assessment that is conducted with limited data (US EPA, 1997). This risk assessment will help provide guidance to government agencies such as Ministry for Primary Industries (MPI), Ministry for the Environment (MfE), Ministry of Health (MoH), Environment Canterbury (ECan) and future researchers.

5.2 Planning and Scoping

The purpose of the planning and scoping stage is to determine who, what and where is at risk. What is the environmental hazard of concern, where does this hazard come from and how does the exposure occur.

Population at Risk

For this risk assessment, the receptors include those who make use of or encounter the groundwater resource. This includes the general population, humans and animals for drinking water and irrigation, and all aquatic species which come into contact with the groundwater also made possible through groundwater surface water exchange.

Chemicals of Concern

For this risk assessment, the chemicals of concern are the emerging organic compounds which were detected in the shallow groundwater wells within the Canterbury region. An overview of the compounds detected, the concentration range and number of detections is presented in Table 5.1 below.

Table 5.1: Chemicals of concern for this risk assessment with concentration range detected in Canterbury groundwater and no. of detections

Compound	Concentration range (ng/L)	No. of detections
BPA	0.3-97.2	18/33
bParaben	1.1-19.4	3/33
BP1	1.4	1/33
BP3	0.4-4.8	5/33
Chlorophene	2.2-33.2	2/33
eParaben	5.4-19.5	2/33
E3	3.0	1/33
mParaben	0.6-71.3	9/33
OMC	1.0	1/33
OP	1.2-453.5	6/33
pParaben	0.9-11.7	4/33
3PBOH	0.5	1/33

Routes of exposure

A contaminant of concern must reach the ecological receptors and be taken up by the receptors for an exposure pathway to be complete. In this case exposure can occur through ingestion of groundwater, irrigation or dermal adsorption. The exposure pathway is the discharge of EOCs into receiving environments where the contaminants are then able to migrate to groundwater and the receptors including aquatic biota, humans, animals and organisms living in groundwater (stygobites) are exposed.

For this risk assessment, exposure was assumed to be 100% of the concentration of contaminants in groundwater. This assumes that 100% of the concentration is bioavailable, concentrations of compounds detected in the particulate phase of groundwater were not included. The exposure duration of these compounds was assumed to be constant due to the pseudo persistence of these compounds [181].

5.3 Problem Formulation

The purpose of the problem formulation phase as stated by the US EPA is "to define an assessment endpoint to determine what ecological entity is important to protect". However due to assessment endpoints often being difficult to measure, related measurement endpoints can be used instead [182]. Measurement endpoints are toxicological endpoints such as the lowest observable effect concentration (LOEC), lethal concentrations (LC_{50}) and chronic effective concentrations (EC_{50}). After assessment endpoints have been selected a conceptual model is developed which visually represents relationships between the environment and exposure stressors.

Assessment Endpoints

For this risk assessment, aquatic toxicological data for the EOCs was compiled from the literature (Table 5.3). Lethal concentration values (LC_{50}), were used to derive predicted no observable adverse effects concentrations (PNOAECs). Where there were no corresponding toxicological data in the literature, predicted toxicity values were used based on quantitative structure activity relationships (QSARS) obtained from Sanderson et al. (2004) [183]. When experimental data is lacking, QSARs have been recognised as reliable models for predicting the toxicity of chemicals [184]. Lethal chronic (LC_{50}) values for compounds were attained using the computer programme Ecosar Application 2.0, this programme is available for free download from the USEPA webpage [185].

Conceptual Model

The conceptual model provides a visual representation of the relationship between the EOCs and the receptors. Initially these compounds are consumed by humans as preservatives or ingredients in foods and personal care products, or as industrial products used in the manufacture of other products. These compounds are then expelled down the drain and end up in WWTPs, once in the municipal waste water system compounds are treated to varying degrees of removal [186]. The treated waste is then discharged into the environment through either irrigation or application of biosolids to land [131]. There are also other sources of EOCs which can cause indirect contamination of groundwater including leakage from sewers and septic tanks [34], landfill leachate [187], runoff from biosolid application [131], storm water runoff [39] and agriculture [1].

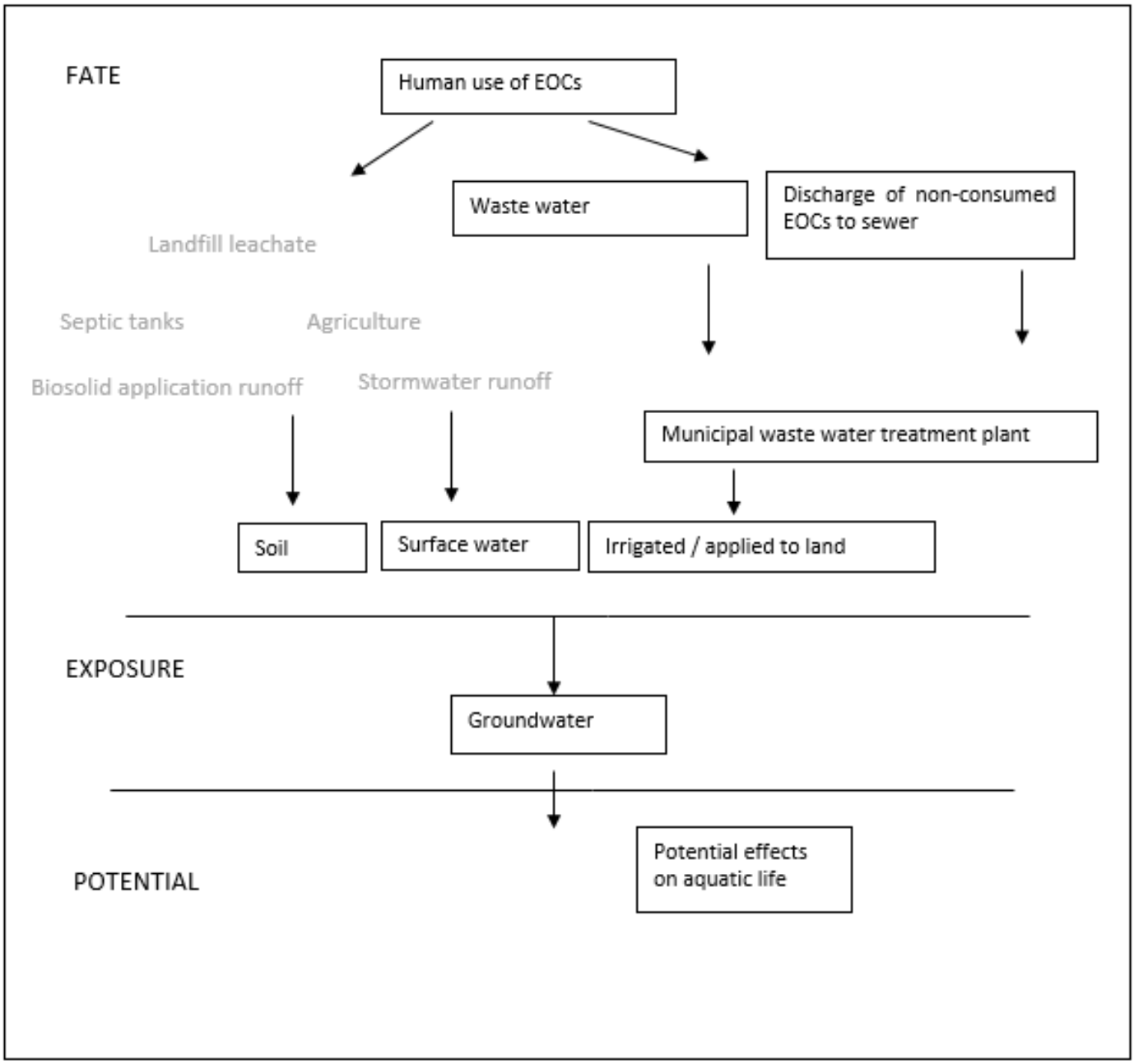


Figure 5.1: Conceptual model of EOCs leaching to groundwater

5.4 Analysis

The purpose of the analysis phase is to determine the exposure of plants and animals and if the level of exposure is likely to cause harmful ecological effects. To do so calculations are made such as derivation of predicted no observable adverse effect concentrations (PNOAEC) values and hazard quotients. Hazard quotients are used to quantify risk and are based on the ratio of contaminant to a screening benchmark.

Deriving Predicted No Observable Adverse Effect Concentrations

As advised by the European Agency for the Evaluation of Medicinal Products (EMEA) 2009 guidelines, LC_{50} values were used to derive PNOAEC values for each compound by applying an assessment factor (Equation 8). The assessment factor is used to account for the degree of uncertainty of the data. Assessment factors recommended by the EMEA are listed (Table 5.2)[188].

Table 5.2: Assessment factors recommended to derive predicted no observable adverse effects concentrations [189]

Available data	Assessment Factor
At least one short-term L(E)C_{50} from each of three trophic levels of the base set (fish, Daphnia and algae)	1000
One long-term no observable effects concentration (NOEC) (either fish or Daphnia)	100
Two long-term NOECs from species representing two trophic levels (fish/and or daphnia and/or algae)	50
Long term NOECs from at least three species (normally fish, daphnia and algae) representing three trophic levels.	10

For this risk assessment the assessment factor applied to the LC_{50} values was 1000. This was chosen based on the limited toxicity data available and for a more conservative approach. The PNOAEC for each compound was calculated by dividing the lowest chronic LC_{50} by the assessment factor 1000. The derived PNOAECs for each compound are listed below (Table 5.3).

Equation 8: Deriving Predicted No Observable Adverse Effect Concentration

$$PNOAEC = \frac{LC_{50}}{Assessment\ Factor}$$

LC_{50} = Lethal chronic dosage for 50% of population

Assessment Factor = 1000

Table 5.3 Summary of derived predicted no observable effect concentration for compounds detected in Canterbury shallow groundwater

Compound	LC_{50} (acute exposure) (mg/L)	PNOAEC (mg/L)	Species	Reference
BPA	1.280	1.28×10^{-3}	Fish	Ecosar database
bParaben	5.3	5.3×10^{-3}	Daphnia magna	[190]
BP1	8.81	8.81×10^{-3}	Daphnid	Ecosar database
BP3	2.40	2.2×10^{-3}	Daphnid	Ecosar database
Chlorophene	1.10	1.1×10^{-3}	Daphnid	Ecosar database
eParaben	18.7	0.0187	Daphnia magna	[190]
E3	6.80	6.8×10^{-3}	Daphnid	Ecosar database
mParaben	24.6	0.0246	Daphnia magna	[190]
OMC	0.234	2.34×10^{-4}	Fish	Ecosar database
OP	0.299	2.99×10^{-4}	Daphnid	Ecosar database
pParaben	12.3	0.0123	Daphnia magna	[190]
3PBOH	22.0	0.022	Daphnid	Ecosar database

Calculating Hazard Quotients

To determine the likelihood of risk, hazard quotients (HQ) were calculated (Table 5.4). Hazard quotients were calculated by dividing the relevant environmental exposure concentration of each compound by their PNOAECs, Equation 9 [191-192].

Table 5.4: Compounds detected in Canterbury shallow groundwater, highest detected concentration, PNOAEC and relevant hazard quotient value.

Compound	Highest detected concentration (ng/L)	Highest detected concentration (mg/L)	PNOAEC (mg/L)	Hazard Quotient (HQ)
BPA	97.2	9.7×10^{-5}	1.3×10^{-3}	7.6×10^{-2}
bParaben	19.4	1.9×10^{-5}	5.3×10^{-3}	3.7×10^{-3}
BP1	1.4	1.4×10^{-6}	8.8×10^{-3}	1.6×10^{-4}
BP3	4.8	4.8×10^{-6}	2.2×10^{-3}	2.0×10^{-3}
Chlorophene	33.2	3.3×10^{-5}	1.1×10^{-3}	3.0×10^{-2}
eParaben	19.5	1.9×10^{-5}	0.0187	1.0×10^{-3}
E3	3.0	3.0×10^{-6}	6.8×10^{-3}	4.5×10^{-4}
mParaben	71.3	7.1×10^{-5}	0.025	2.9×10^{-3}
OMC	1.0	9.7×10^{-7}	2.3×10^{-4}	4.1×10^{-3}
OP	453.5	4.5×10^{-5}	3.0×10^{-4}	1.5
pParaben	11.7	1.2×10^{-5}	0.012	9.5×10^{-4}
3PBOH	0.5	4.6×10^{-7}	0.022	2.1×10^{-5}

Equation 9: Calculating the hazard quotient

$$HQ = \frac{EEC}{PNOAEC}$$

5.5 Risk Characterization

Results – Hazard Quotients

In total, there were 13 EOCs detected from the groundwater sampled across the Canterbury region. The hazard quotient values were calculated based on the maximum detected values of these compounds. A hazard quotient between 0-0.9 is indicative of a low risk, that between 1-9 a medium risk and over 10 is considered a high risk. The majority of hazard quotient values were well below 1, this indicates an extremely low level of risk regarding most compounds. However, the hazard quotient for OP was found to be 1.5 this is indicative of a medium risk. Chlorophene and BPA hazard quotient values were above 0 but still low at 0.030 and 0.076 respectively this is indicative of a low risk.

Implications

Octylphenol (OP) is an industrial compound used to manufacture many products including rubber materials, paints, adhesives, coatings and inks, it is also present in household and industrial detergents and surfactants and present in some personal care products including hair products, cosmetics, soap and skincare [193] [194]. Octylphenol enters the environment through wastewaters, due to incomplete removal during wasterwater treatment processes[195]. Octylphenol is not currently known to be used in agriculture in New Zealand. Increasing concentrations of OP in the environment could cause restrictions of its use in the future.

5.6 Human Health Risk Assessment

The maximum concentration detected of each EOC detected in Canterbury groundwater was compared to a derived Drinking Water Guideline Level (DWGL), this is a concentration believed to be below that where adverse effects due to a lifetime of exposure occur.

5.6.1 Calculating Acceptable Daily Intake

The acceptable daily intake (ADI) is defined as the dose which can be ingested over a lifetime with negligible risk or adverse effects (Equation 10). It is calculated with the use of NOAEL and LOAEL values from the literature, a safety factor is applied which accounts for the level of uncertainty, in this study 1000 was applied.

Equation 10: Calculating the acceptable daily intake (ADI)

$$ADI\ \left(\frac{mg}{kg\ day}\right) = \frac{NOAEL\ or\ LOAEL}{SF}$$

SF= Safety Factor applied = 1000

5.6.2 Derivation of Drinking Water Guideline Levels

At the present time there are no official DWGLs set for the compounds analysed in this study. Therefore, DWGLs were calculated following guidelines from the World Health Organization (WHO, 2011) [196]. The DWGL for each compound was calculated (Equation 11) where ADI is the Acceptable Daily Intake, BW is the body weight (70 kg), P is the fraction of substance ingested through water consumption (assumed to be 0.1 for marketed substances and industrial use substances [197]) and V is the daily volume of water ingested (2 L) [198]. The calculated DWGLs are presented in Table 5.5.

Equation 11: Derivation of drinking water guideline level

$$DWGL\left(\frac{\mu g}{kg}day\right) = ADI \times BW \times P \times \frac{10^3}{V}$$

5.6.3 Calculating hazard quotients

To evaluate the risk compounds detected pose to humans, hazard quotient values were calculated (Equation 12) where EOC concentration is the maximum detected concentration in groundwater and DWGL, is the corresponding Drinking Water Guideline Level. A HQ below 1 is indicative of no risk to human health, a HQ above 1 requires further investigation.

Equation 12: Calculating hazard quotients to assess risk posed by EOCs detected to human health

$$HQ = \frac{EOC\ concentration}{DWGL}$$

Table 5.5: EOCs detected in Canterbury groundwater, maximum detected concentrations, NOAEL and LOAEL values from the literature, with respective acceptable daily intakes, drinking water guideline limits and relative hazard quotients

Compound	Maximum detected concentration (ng/L)	NOAEL/LOAEL (mg/kg/bw)	Reference	ADI (ug/kg*d)	DWGL (ug/L)	HQ
BPA	97.2	50	[199]	50	175	5.5×10^{-4}
bParaben	19.4	100	[200]	100	350	5.5×10^{-5}
BP1	1.4	6	[201]	6	21	6.6×10^{-5}
BP3	4.8	200	[202]	200	700	6.8×10^{-6}
Chlorophene	33.2	10	[203]	10	35	9.5×10^{-4}
eParaben	19.5	1000	[204]	1000	3500	5.6×10^{-6}
E3	3.0	*				
mParaben	71.3	1000	[205]	1000	3500	2.0×10^{-5}
OMC	1.0	500	[206]	500	1750	5.7×10^{-7}
OP	453.5	400	[207]	400	1400	3.2×10^{-4}
pParaben	11.7	3.3	[208]	3.3	11.55	1.0×10^{-3}
3PBOH	0.5	200	[209]	200	700	7.0×10^{-7}

NOAEL= No observable adverse effect level

LOAEL= Lowest observable adverse effect level

ADI= Acceptable daily intake

DWGL= Drinking water guideline limit

HQ= Hazard Quotient

*= No literature available

5.6.4 Results from Human Health Risk Assessment

The calculated hazard quotient values are reported in Table 5.5 and show negligible risks for human health. The HQ values were well below 1 for all the compounds detected in groundwater ranging from 7.0 x 10^{-7} for 3PBOH to 1.0 x 10^{-3} for pParaben. No toxicity data for estriol was available in the literature for the calculation of its hazard quotient. It is important to note that most of the groundwater wells sampled are not used for drinking water.

5.7 Conclusion

The ecological risk calculated in this assessment is likely an overestimation due to the highest detected environmental concentration being compared with the lowest reported toxicity values which have the highest uncertainty factor of 1000 applied to them. It is recommended by regulatory guidance documents that compounds with HQs > 1 should be further investigated. Of the 12 HQs calculated, only 1 EOC, OP had a HQ greater >1. Further investigation would be required to determine the source of this compound and whether the detected concentration is likely to be a one off. The human health risk assessment shows negligible risks for human health, the HQs were all well below 1 for all the compounds detected. No further investigation is required at this point in time regarding these compounds and human health.

CHAPTER SIX

FINAL CONCLUSIONS

AND

RECOMMENDATIONS

6 Final Conclusions and Recommendations

6.1 Summary of findings

The objectives of this thesis were to (a) Develop and validate a novel method for the extraction and clean-up of EOCs from soil and particulate samples; (b) analyse soil, dairy effluent and WWTP effluent samples as these are potential sources of contamination to groundwater of EOCs; (c) determine the concentrations of EOCs in a selection of Canterbury groundwater wells across two seasons; and (d) undertake a risk assessment based upon the current concentrations of EOCs detected in Canterbury groundwater. This was the first known study in New Zealand to analyse for EOCs in groundwater.

The novel method developed for the extraction and clean-up of EOCs from soil and particulates used an ultrasonic extraction, followed by EMR dispersive solid phase extraction and polish for clean-up. This new method obtained good recoveries for target analytes with recoveries ranging between 70% and 137% for soil and 66% and 121% for suspended particulates. Analytes with recoveries outside this range included E1, NP and OPP and therefore were not included in the results.

Soil samples from six sites were collected, these sites were all areas where either farm effluent or wastewater effluent were irrigated to land. Effluent samples were also collected at five sites, three were WWTPs and two were from dairy farms. These samples utilised the newly developed method of extraction and clean-up. From the collected soil samples 5/25 target analytes were detected, including mParaben, OPP, mTric, EE2 and Androstenedione, the concentrations ranged from 0.18 μg/kg for OPP to 152.5 μg/kg for EE2. For the effluent samples collected 13/25 target analytes were detected in the dissolved phase, (mParaben, eParaben, OPP, pParaben, 4MBC, BP3, Tric, BP1, BPA, E1, E3, Testosterone and Androstenedione). Concentrations detected in the dissolved phase were compared to international values detected in influent and effluent. The concentrations detected in this study were comparable to concentrations detected in effluent samples overseas. Sample WW2 was sampled prior to any wastewater treatment and had high concentrations of mParaben, eParaben and pParaben and was found to contain similar

concentrations to overseas influent. Very few studies have analysed the particulate phase of effluent samples, apart from one New Zealand study in Gisborne [155]. The data from the current study was found to be of similar magnitude of concentration as the Gisborne study.

A selection of 18 shallow groundwater wells were sampled across two seasons and analysed for 25 EOCs (Chapter 4). Samples were filtered and the dissolved phase and suspended particulate phase were analysed separately. The results from these two sampling rounds detected 13 of the 25 target EOCs, maximum concentrations ranged from 0.461-453.5 ng/L. Of the 33 wells sampled 26/33 groundwater wells had at least one detection of a target analyte, BPA was the most frequently detected compound detected in 55% of groundwater samples. The wells in proximity to WWTPs had the greatest number of EOC detections with detections in 100% of samples. Concentrations detected in the dissolved phase of groundwater were of similar magnitude to the lower range of concentrations detected overseas. There was a seasonal trend for the wells with the greatest number of EOC detections during the spring season. Wells were grouped into depth categories to determine whether there was a correlation between depth and contamination. Highest levels of contamination in wells with a depth less than 8 metres, these wells were also closest to WWTPs. Eleven of the thirty-four particulate samples had at least one detection of a target analyte with maximum concentrations ranging from 1.43 ng/L for E3 to 22.3 ng/L for BPA. As for the dissolved phase of groundwater BPA was also the most detected analyte in the particulate phase. There was a seasonal trend for the particulate phase of groundwater samples as most of detections were during the spring season.

A risk assessment was undertaken based on the 13 target analytes detected in Canterbury groundwater. Predicted no observable effect concentrations (PNOAEC) were derived based on LC_{50} values found in the literature and quantitative structure activity relationships, an assessment factor of 1000 was applied by dividing respective LC_{50} values by 1000. Hazard quotients for each compound were assigned by dividing their maximum concentrations detected in groundwater by the PNOAEC. The majority of hazard quotient values were well below 1 indicating a low level of risk, however, the hazard quotient of OP was found to be 1.5 indicative of a medium risk. Further research is required to determine the source of OP and whether the concentration detected is a

one off.

Human health risk was assessed by comparing the maximum concentrations detected in Canterbury groundwater with derived drinking water guideline levels. Drinking water guideline levels (DWGL) were derived from acceptable daily intake values for each compound, average body weight of humans, fraction of substance ingested and average daily volume of water consumed by humans. HQs were then derived by dividing the maximum detected EOC concentration by the DWGL. A HQ<1 was indicative of no risk to human health. All hazard quotient values were well below 1.

In conclusion, this study has explored two major sources of EOCs to groundwater, soil and effluent, samples collected have shown the presence of these compounds at similar concentrations to that found in overseas studies. This study was the first to investigate EOCs in groundwater in New Zealand. Shallow groundwater wells across Canterbury do contain EOCs at very low ng/L concentrations. The current concentrations detected pose a low ecological risk with OP requiring further investigation, there is no risk to human health presented at the current levels detected.

6.2 Limitations of this study

This study was carried out over 12 months, therefore there was a limited space of time to fit sampling and lab analysis required. It would have been ideal to have also sampled effluent and soil over both the spring and summer season as it is highly likely the concentrations and detection of EOCs will vary across seasons.

This study sampled wells based on those thought to be contaminated therefore, presents a worst-case scenario, therefore this data does not depict an average scenario of Canterbury. A much greater sample size would be needed to illustrate the true extent of these contaminants for the whole of Canterbury.

This study did not include a deconjugation step prior to analysis of steroid hormones, this may mean the concentration of hormones may be greater than what was detected in this study.

6.3 Implications

The main implications of this research are for councils and policy makers considering the inclusion of EOCs in future groundwater monitoring programmes and guideline limits. Due to the current concentrations in groundwater portraying a low level of risk from wells which depict a worst-case scenario level of contamination, it would appear monitoring of these compounds in groundwater may not be necessary at this stage.

6.4 Recommendations

Further studies focusing on a single WWTP site or intensive farming site would allow for a more in-depth understanding of the movement of EOCs through the environment by implementing monthly sampling of influent, effluent, irrigated soil and groundwater monitoring wells. This would help show which compounds are removed during which phases of treatment. More in-depth characterisation of the soils would also be useful in determining partitioning of compounds between the soil and groundwater.

Further laboratory studies are also required to investigate the combined toxicity of EOCs to be able to assess the overall risk more accurately.

Further experimental laboratory studies should be carried out to determine whether OP may also be leaching along with BPA from PVC well casings due to many wells in this study containing PVC.

There is a need to improve analytical methods for steroid hormones by inclusion of a deconjugation step for hormones. Improvement is also required to be able to quantify OPP and E1 in samples due to unacceptable recoveries for them obtained in this study.

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8 Appendices

Appendix 1: Information and Consent Sheet for Well Owners

Email: rebecca.vanderkrogt@pg.canterbury.ac.nz

6th September 2017

Emerging Contaminants in the environment - groundwater

My name is Rebecca van der Krogt this year I am undertaking a survey of shallow groundwater wells across Canterbury as part of my Masters in Environmental Sciences at the University of Canterbury.

This study will involve collecting and analysing groundwater samples. Well water will be tested for a range of emerging contaminants including uv-filters, hormones, parabens, plasticizers and organic carbon. I will also test the temperature, conductivity, dissolved oxygen and pH of the water in each well.

Any information supplied and data collected will be under a condition of anonymity and on this basis the University of Canterbury will not release it to third parties. Additionally, you have the right to withdraw from the project at any time, including withdrawal of any information provided.

The information gathered will be used to prepare a thesis which is a public document that will be made available through the University of Canterbury Library, seminar and subsequent scientific publications. Individual sites and landowners will not be identified. You will be sent a copy of the results for your property.

This research is being carried out under the supervision of Professor Sally Gaw, who can be contacted at sally.gaw@canterbury.ac.nz

Thank you for your time in reading this information and considering participation in this research, if you have any further questions or require further information, please do not hesitate to contact me.

If you agree to participate in this study, you are asked to complete the consent form and return by either scanning and emailing to rebecca.vanderkrogt@pg.canterbury.ac.nz or in person. Sampling of your well will be carried out at the same time as Environment Canterbury's sampling.

Kind regards

Rebecca van der Krogt

Emerging Contaminants in the environment – groundwater

Consent form for well owners

	Initial
I have received an explanation of this research project and have had the opportunity to ask any questions I may have. YES/NO	
I understand that any information I provide will be kept confidential and that any published results will not identify people or companies. YES/NO	
I understand that a thesis is a public document that will be made available through the University of Canterbury Library. YES/NO	
I understand that all raw data collected for this study will be stored on a password protected computer and will be destroyed after 5 years. YES/NO	
I understand that I can receive a report on the findings of the study by contacting the researcher at the conclusion of the project. YES/NO	
I understand that I am able to contact the researcher Rebecca van der Krogt at Rebecca.vanderkrogt@pg.canterbury.ac.nz or her supervisor Associate Professor Sally Gaw at sally.gaw@canterbury.ac.nz for further information. YES/NO	

By signing below, I agree to participate in this research project.

Name_____ Date_____

Signature_____

Appendix 2: In depth summary of each groundwater site

Well code: W12	Depth: 8.00m	Diameter: 50mm	Casing: PVC
Locality: Ashburton			
Description of surroundings: This well is in very close proximity (less than 5 metres) to oxidation ponds for the treatment of municipal wastewater			

Well code: W11	Depth: 7.2m	Diameter: 50mm	Casing: PVC
Locality: Ashburton			
Description of surroundings: This well is up gradient of oxidation ponds (approximately 78 metres), human effluent discharge to left of well (approximately 65 metres). Well is downstream of two human effluent discharges (approximately 792.7 and 916.9 metres).			

Well code: W22	Depth: 8.00m	Diameter: 50mm	Casing: PVC
Locality: Ashburton			
Description of surroundings: This well is up gradient of oxidation ponds (approximately 634 metres), human effluent discharge to right of well (approximately 307 metres)			

Well code: W21	Depth: 7.00m	Diameter: 50mm	Casing: PVC
Locality: Ashburton			
Description of surroundings: Well is down gradient of oxidation ponds (approximately 2,055 metres). Well is downstream of two human effluent discharges (at approximately 227 and 771 metres)			

Well code: W33	Depth: 22.20m	Diameter: 350mm	Casing: Unknown
Locality: Harewood			
Description of surroundings: Suburban rural fringe environment, no sources of contamination or discharges nearby, previously used for community supply, decommissioned during study due to shallow depth			

Well code: W44	Depth: 6.00m	Diameter: Unknown	Casing: Unknown
Locality: Springfield			
Description of surroundings: Approximately 280 meters from the Rakaia gorge, rural farming area, used for public drinking water supply			

Well code: W55	Depth: 3.00m	Diameter: Unknown	Casing: Unknown
Locality: Methven			
Description of surroundings: Surrounded by farms situated in rural area, within 400 meters from the Rakaia river, two dairy farm effluent discharges consented within 2km radius, used for public drinking water supply			

Well code: W66	Depth: 4.00m	Diameter: Unknown	Casing: Steel
Locality: Mt Somers			
Description of surroundings: Rural location, no nearby discharges, used for public drinking water supply			

Well code: W71	Depth: 3.30m	Diameter: 100mm	Casing: Unknown
Locality: Amberley			
Description of surroundings: Wastewater treatment plant monitoring well,			

Well code: W73	Depth: 3.30m	Diameter: 100mm	Casing: Unknown
Locality: Amberley			
Description of surroundings:			

Well code: W13	Depth: 11.50m	Diameter: 150mm	Casing: Steel
Locality: Stavely Ashburton			
Description of surroundings: Rural location, consent to discharge human effluent on same property as well approximately 120 metres away, well used for domestic supply.			

Well code: W14	Depth: 10.00 m	Diameter: 150mm	Casing: Steel
Locality: Ashburton			
Description of surroundings: Rural location, human effluent discharge approximately 1km from well			

Well code: W15	Depth: 9.75m	Diameter: 100mm	Casing: Steel
Locality: Ashburton			
Description of surroundings: Rural location human effluent discharge 120m from well			

Well code: W16	Depth: 7.30m	Diameter: 300mm	Casing: Unknown
Locality: Hanmer Springs			
Description of surroundings: Rural area			

Well code: W17	Depth: 6.00m	Diameter: 50mm	Casing: PVC
Locality: Waiau			
Description of surroundings: Rural area			

Well code: W18	**Depth: 9.10m**	**Diameter: 150mm**	**Casing: PVC**
Locality: Hurunui/Waiau			
Description of surroundings: Rural area			

Well code: W23	**Depth: 9.00m**	**Diameter: 100mm**	**Casing: Steel**
Locality: Culverden			
Description of surroundings: Rural area			

Well code: W24	**Depth: 5.00m**	**Diameter: 51mm**	**Casing: Steel**
Locality: Culverden			
Description of surroundings: Rural area			

Appendix 3: EOC concentrations for all samples

Table 8.1: Emerging Organic Contaminants detected in groundwater samples during the first round of sampling (DP) (ng/L), particulate phase (PP) (ng/L) and (μg/Kg), total (DP + PP (ng/L)

Analytes	W11				W12				W21				W22				W33			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	19.4	0.19	1.41	17.6	10.0	0.47	2.30	10.47	71.3	-	-	71.3	-	-	-	-	-	-	-	-
eParaben	5.4	-	-	5.5	-	-	-	-	19.5	-	-	19.5	-	-	-	-	-	-	-	-
OPP	1.1	-	-	1.1	3.8	-	-	3.8	7.2	-	-	7.2	2.4	-	-	2.4	-	-	-	-
OP	-	-	-	-	453.5	-	-	453.5	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	2.7	-	-	2.7	-	-	-	-	11.7	-	-	11.7	-	-	-	-	-	-	-	-
bParaben	4.3	-	-	4.3	-	-	-	-	19.4	-	-	19.4	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	33.2	-	-	33.2	-	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP3	-	0.39	2.93	0.39	-	-	-	-	3.7	0.37	2.77	4.07	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	0.39	1.94	0.39	-	-	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	-	5.58	42.0	5.58	54.5	0.28	1.37	54.78	6.2	-	-	6.2	-	-	-	-	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	3.0	-	-	3.0	-	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	1.27	9.57	1.27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8.1: continued

Analytes	W55				W66				W44				W13				W14			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	-	-	-	-	-	0.31	2.36	0.31	-	0.43	3.20	0.43	-	-	-	-	-	-	-	-
eParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OPP	-	-	-	-	-	-	-	-	-	0.49	3.70	0.49	-	-	-	-	0.00875	-	-	0.0087
OP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.461	-	-	0.461
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	4.82	-	-	4.82	-	-	-	-
BP3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP-1	-	0.96	4818.8	0.96	-	1.15	8.67	1.15	-	-	-	-	-	-	-	-	1.47	-	-	1.47
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	9.79	0.78	3907.5	10.57	-	8.07	60.7	8.07	-	-	-	-	8.74	-	-	8.74	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8.1: continued

Analytes	W15				W16				W17				W18				W23			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.49	829.6	2.49
eParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OPP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.52	507.3	1.52
OP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.70	566	1.70
bParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.67	555.1	1.67
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.26	754.5	2.26
BP3	1.81	-	-	1.81	-	-	-	-	-	-	-	-	-	-	-	-	-	1.87	623.9	1.87
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.10	702.9	2.10
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	4.43	-	-	4.43	1.97	-	-	1.97	1.91	-	-	1.91	6.33	0.47	2342.5	6.8	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.02	1005.2	3.02
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8.1: continued

Analytes	W24			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-
mParaben	-	-	-	-
eParaben	-	-	-	-
OPP	-	-	-	-
OP	-	-	-	-
pParaben	-	-	-	-
bParaben	-	-	-	-
3PBOH	-	-	-	-
Chlorophene	-	-	-	-
NP	-	-	-	-
4MBC	-	-	-	-
BP3	2.07	-	-	2.07
mTric	-	-	-	-
Tric	-	-	-	-
BP-1	-	-	-	-
bzParaben	-	-	-	-
BPA	-	-	-	-
OMC	-	-	-	-
E2	-	-	-	-
EE2	-	-	-	-
E3	-	-	-	-
Testosterone	-	-	-	-
Androstenedione	-	-	-	-
17a Estradiol	-	-	-	-

Table 8.2: Emerging Organic Contaminants detected in groundwater samples during the second round of sampling (DP), particulate phase (PP) and total DP + PP

Analytes	W71				W73				W11				W12				W21			
	DP (ng/L)	PP (ng/L)	PP (µg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (µg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (µg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (µg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (µg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
mParaben	-	-	-	-	6.05	-	-	6.05	-	NT	-	-	-	-	-	-	6.02	-	-	6.02
eParaben	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
OPP	7.76	-	-	7.76	3.63	0.44	9.28	4.07	5.61	NT	-	-	1.32	-	-	1.32	-	-	-	-
OP	-	-	-	-	-	-	-	-	1.54	NT	-	-	144.9	-	-	144.9	1.07	-	-	1.07
pParaben	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	2.15	NT	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
BP3	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-	1.43	NT	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
BPA	44.1	5.02	930.1	49.12	97.3	-	-	97.3	0.54	NT	-	-	10.0	-	-	10.0	0.26	-	-	0.26
OMC	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	0.97	-	-	0.97
E2	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	0.36	7.47	0.36	-	NT	-	-	-	-	-	-	-	-	-	-
Testosterone	-	0.36	66.0	0.36	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	0.31	57.5	0.31	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	NT	-	-	-	-	-	-	-	-	-	-

Table 8.2 continued

Analytes	W22				W55				W66				W44				W13			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	13.3	-	-	13.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
eParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OPP	-	-	-	-	-	-	-	-	-	-	-	-	-	0.42	1.86	0.42	1.27	-	-	1.27
OP	1.43	-	-	1.43	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	2.33	-	-	2.33	-	-	-	-	-	-	-	-	0.95	-	-	0.95	-	-	-	-
bParaben	1.08	-	-	1.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP3	0.40	-	-	0.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	-	-	-	-	-	-	-	-	2.25	-	-	2.25	-	-	-	-	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8.2 continued

Analytes	W14				W15				W16				W17				W18			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
mParaben	-	-	-	-	4.19	-	-	4.19	-	-	-	-	0.65	-	-	0.65	-	NT	-	-
eParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
OPP	-	-	-	-	1.83	-	-	1.83	3.04	-	-	3.04	5.04	-	-	5.04	-	NT	-	-
OP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
pParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
bParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
BP3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
BP-1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
BPA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
E3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	NT	-	-

Table 8.2: Continued

Analytes	W23				W24			
	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/Kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-
mParaben	2.05	-	-	2.05	-	-	-	-
eParaben	-	-	-	-	-	-	-	-
OPP	3.53	-	-	3.53	-	-	-	-
OP	6.81	-	-	6.81	-	-	-	-
pParaben	1.25	-	-	1.25	-	-	-	-
bParaben	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-
BP3	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-
BPA	2.96	-	-	2.96	2.55	-	-	2.55
OMC	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-

Table 8.3:Emerging Organic Contaminants detected in soil samples (μg/kg)

Analyte	S1	S1 dup	S11	S11 dup	S2	S22	S22 dup	S3	S3 dup	S4	S4 dup
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-
mParaben	-	2.15	-	-	4.73	39.69	24.00	2.53	3.33	1.64	3.21
eParaben	-	-	-	-	-	-	-	-	-	-	-
OPP	0.35	0.20	-	-	0.37	-	-	-	-	-	-
OP	-	-	-	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-
BP3	-	-	-	-	-	-	-	-	-	-	-
mTric	27.27	1.06	9.70	11.61	2.08	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-
BPA	-	-	-	-	-	-	-	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-
E1	-	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	14.48	290.53	-	-	4.17	-
E3	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	0.75	-	7.20	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-

Table 8.4: Emerging Organic Contaminants detected in effluent

Analytes	WW1				WW2				WW3				DS1				DS2			
	DP (ng/L)	PP (ng/L)	PP (μg/kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/kg)	Total (ng/L)	DP (ng/L)	PP (ng/L)	PP (μg/kg)	Total (ng/L)
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	-	-	-	-	811.8	3.11	1.74	814.91	-	-	-	-	48.4	-	-	48.4	-	-	-	-
eParaben	-	-	-	-	187.7	-	-	187.7	-		-	-	-	-	-	-	-	-	-	-
OPP	40.0	-	-	40.0	5.73	-	-	5.73	-	0.6	37.9	640	-	-	-	-	-	-	-	-
OP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	219.3	-	-	219.3	-	-	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	47.2	26.4	47.2	-	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	38.3	21.42	38.3	246.8	-	-	246.8	-	-	-	-	-	-	-	-
BP3	-	-	-	-	56.7	-	-	56.7	42.5	-	-	42.5	-	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	146.3	334.9	187.48	481.2	89.0	27.9	1667.6	116.9	-	-	-	-	-	-	-	-
BP-1	-	1.50	30.4	1.50	-	-	-	-	-	0.8	46.4	0.8	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	-	-	-	-	11.0	-	-	11.0	16.4	1.7	103.1	18.1	86.8	-	-	86.8	-	-	-	-
OMC	-	2.69	54.5	2.69	-	459.9	257.5	459.9	-	16.4	979.8	16.4	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	58.3	-	-	58.3	5.52	-	-	5.52	-	30.4	197.3	30.4	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	83.7	-	-	83.7	-	-	-	-
Androstenedione	6.07	-	-	6.07	-	-	-	-	1.81	-	-	1.81	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	8.4	54.7	8.4	-	-	-	-

Appendix 4: Data on analytical duplicates and blanks

Table 8.6 Analytical duplicates for dissolved phase of groundwater (ng/L) across both seasons

Analyte	W12	W12dup	W55	W55dup	W16	W16dup	W14	W14dup	W55	W55dup
chloroxylenol	-	-	-	-	-	-	-	-	-	-
mParaben	13.5	6.49	-	-	-	-	1.038	-	-	-
eParaben	-	-	-	-	-	-	-	-	-	-
OPP	3.67	3.85	-	-		-	4.59	-	-	-
OP	388.6	518.5	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-
Chlorophene	33.4	33.0	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-
BP3	-	-	-	-	-	-	-	1.11	-	-
mTric						-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-
BPA	67.3	59.3	14.2	9.2	-	-	1.41	1.54	-	-
OMC	-	-	-	-	-	-	-	-	-	-
E1	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-
E3	2.3	3.8	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-

Table 8.7 Analytical duplicates for dissolved phase of groundwater (ng/L) across both seasons

Analyte	W22	W22dup	W17	W17dup	W13	W13dup	W73	W73dup
chloroxylenol	-	-	-	-	-	-	-	-
mParaben	11.4	15.1	1.29	-	-	-	6.14	5.96
eParaben	-	-	-	-	-	-	-	-
OPP	-	-	5.52	4.56	1.01	1.52	4.16	3.10
OP	0.86	1.16	-	-	-	-	-	-
pParaben	1.95	2.71	-	-	-	-	-	-
bParaben	1.02	1.14	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-
BP3	0.81	-	-	-	-	-	-	-
mTric	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-
BP-1	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-
BPA	-	-	-	-	-	-	100.4	94.1
OMC	-	-	-	-	-	-	-	-
E1	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-

Table 8.8 Analytical duplicates for particulate phase of groundwater (μg/kg) across both seasons

Analyte	W12	W12dup	W55	W55dup	W33	W33dup	W16	W16dup	W14	W14dup	W22	W22dup	W17	W17dup
chloroxylenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mParaben	1.91	2.69	-	-	-	-	-	-	-	-	-	-	-	-
eParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OPP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-
bParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3PBOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NP	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4MBC	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mTric	-	-	-	-		-	-	-	-	-	-	-	-	-
Tric	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BP-1	3.89	-	4818.6	-	-	-	-	-	-	-	-	-	-	-
bzParaben	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Testosterone	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Androstenedione	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17a Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8.9 Analytical blanks extracted alongside dissolved phase of groundwater during first round of sampling (ng/L)

	1		2		3		4		5	
Analytes	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank
Chloroxylenol									4.2	
mParaben									1.6	
OPP	0.6				0.8		1.8		4.6	
3PBOH									0.9	
mTric									1.1	
BPA	8.8				1.9		1.4	1.3	1.9	
OMC		0.9								

1 Extracted alongside = W11, W12, W21, W22

2 Extracted alongside = W33

3 Extracted alongside =W44, W55, W66

4 Extracted alongside = W16, W17, W18, W23, W24

5 Extracted alongside = W13, W14, W15

Table 8.10 Analytical blanks extracted alongside dissolved phase of groundwater during second round of sampling (ng/L)

	1		2		3		4		5	
Analytes	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank	Field blank	Lab blank
OPP	2.2			0.3					0.2	
pParaben					1.1					
BPA		1.9	30.7	31.7	1.9	1.5	60.3	11.6	1.6	4.1

1 Extracted alongside = W11, W12, W21, W22

2 Extracted alongside = W71, W73

3 Extracted alongside =W44, W55, W66

4 Extracted alongside = W16, W17, W18, W23, W24

5 Extracted alongside = W13, W14, W15

Table 8.11 Analytical blanks extracted alongside suspended phase of groundwater and effluent (ng/L)

	Batch 1		Batch 2		Batch 3		Batch 4		Batch 5		Batch 6		Batch 7		Batch 8	
Analytes	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank	Solvent blank	Filter blank
BPA	0.8			3.3		6.4		13.2		13.2	7.6	14.7			3.3	
4MBC			5.4													

Batch 1 Extracted alongside = W11(1), W12(1), W21(1), W22(1), W66(1), W44(1)

Batch 2 Extracted alongside = W55(1), W339(1), W18(1), W16(1), W17(1)

Batch 3 Extracted alongside = W23(1), W24(1), W18(1), W15(1), W14(1), W13(1)

Batch 4 Extracted alongside = W66(2), W44(2), W55(2), W11(2), W21(2), W22(2),

Batch 5 Extracted alongside = W22(2), W12(2), WW2

Batch 6 Extracted alongside = DS1, W22(2), W12(2)

Batch 7 Extracted alongside = W71(2), W73(2), W16(2), W17(2), W23(2), W24(2)

Batch 8 Extracted alongside = W13(2), W14(2), W15(2), WW1, WW3

(1) = season 1
(2) = season 2

Table 8.12 Analytical blanks extracted alongside dissolved phase of effluent (ng/L)

	1	2	3	4	5
Analytes	Cartridge blank	Cartridge blank	Cartridge blank	Cartridge blank	Cartridge blank
OPP			3.1		
3PBOH			3.1		
pParaben			2.7		
BPA	12.5	6.4	8.2	7.7	6.2

1 = Extracted alongside WW3

2 = Extracted alongside WW1

3 = Extracted alongside WW2

4 = Extracted alongside DS1

5 = Extracted alongside DS2

Table 8.13: Internationally reported concentrations of EOCs in soil

Compound	Use	Range (µg kg^{-1})	Reference
Androstenedione	Natural hormone	0.07-1.42	[139]
Bisphenol A (BPA)	Industrial chemical	0.7-44.5	[210]
Butyl paraben (bParaben)	Preservative	0.48-1.02	[141]
Benzophenone-1 (BP-1)	UV-filter	0.26-0.61	[211]
Benzophenone-3 (BP-3)	UV-filter	0.5-27	[211]
Benzyl paraben	Preservative	0.33-1.83	[161]
Chlorophene	Preservative	*	
Chloroxylenol	Antiseptic/disinfectant	*	
Ethyl paraben (eParaben)	Preservative	0.75-1.23	[141]
Estrone (E1)	Natural hormone	0.52-7.93	[139]
17β-estradiol (E2)	Natural hormone	19.1	[212]
17α-ethinyl-estradiol (EE2)	Synthetic hormone	0.28-1.20	[139]
Estriol (E3)	Natural hormone	*	
Methyl paraben (mParaben)	Preservative	1.21-8.04	[141]
Methyl Triclosan	Antimicrobial	*	
Nonylphenol (NP)	Industrial Chemical	0.45-10	[141, 213]
2-ethylhexyl-p-methoxycinnamate (OMC)	UV-filter	*	
4-tert-Octylphenol (OP)	Industrial Chemical	190-6500	[214]
***o*-phenylphenol (OPP)**	Industrial Chemical	*	
Propyl paraben (pParaben)	Preservative	0.63-1.34	[161]
Testosterone	Natural hormone	0.05-7.3	[139, 212]
Triclosan	Antimicrobial	*	
3PBOH	Metabolite of insecticide	*	
4 - methylbenzylidene camphor (4-MBC)	UV-filter	*	
17α-estradiol	Metabolite of 17β-estradiol	14.8	[212]

* = Data not available in the literature

Table 8.14: Internationally reported concentrations of EOC's in WWTPs

Compound	Use	Matrix	Range (ng L^{-1})	Reference
Androstenedione	Natural hormone	Influent	<1-14040	[150]
		Effluent	<1-7720	[150]
Bisphenol A (BPA)	Industrial chemical	Influent	80-4980	[54]
		Effluent	6-3642	[54]
Butyl paraben (bParaben)	Preservative	Influent	9.7-864	[147, 152, 153]
		Effluent	<0.2-83	[215, 147, 149, 152]
Benzophenone-1 (BP-1)	UV-filter	Influent	31-700	[142, 143, 144]
		Effluent	<2-41	[142, 143, 145]
Benzophenone-3 (BP-3)	UV-filter	Influent	11-7,800	[65, 143, 144]
		Effluent	3-2,196	[142, 146, 65]
Benzyl paraben	Preservative	Influent	*	
		Effluent		
Chlorophene	Preservative	Influent	*	
		Effluent		
Chloroxylenol	Antiseptic/disinfectant	Influent	*	
		Effluent		
Ethyl paraben (eParaben)	Preservative	Influent	2.2-719	[147, 216]
		Effluent	<0.3-69	[142, 147, 149]
Estrone (E1)	Natural hormone	Influent	<10-670	[150]
		Effluent	<0.1-147	[150, 217]
17β-estradiol (E2)	Natural hormone	Influent	2.4-161.6	[150]
		Effluent	0.2-158	[150]
17α-ethinyl-estradiol (EE2)	Synthetic hormone	Influent	<0.2-70	[218]
		Effluent	<0.3-7.5	[218]
Estriol (E3)	Natural hormone	Influent	10-660	[150]
		Effluent	0.43-151	[150]
Methyl paraben (mParaben)	Preservative	Influent	12.5-9,880	[147, 216]
		Effluent	2.1-423	[142, 147]
Methyl Triclosan	Antimicrobial	Influent	<1-307	[219]
		Effluent	<2-51	[219]
Nonylphenol (NP)	Industrial Chemical	Influent	70-25,000	[147, 152, 220]
		Effluent	<29-3,210	[147, 152, 220]
2-ethylhexyl-p-methoxycinnamate (OMC)	UV-filter	Influent	54-19,000	[146, 151]

		Effluent	<10-177	[65, 148]
4-tert-Octylphenol (OP)	Industrial Chemical	Influent	<1.2-4,500	[147, 152, 220]
		Effluent	<1.2-3,949	[147, 142, 152]
***o*-phenylphenol (OPP)**	Industrial Chemical	Influent	*	
		Effluent		
Propyl paraben (pParaben)	Preservative	Influent	43-2,640	[147, 152, 153]
		Effluent	<0.25-95	[147, 142, 154]
Testosterone	Natural hormone	Influent	7.9-1261	[150]
		Effluent	<0.3-20	[150]
Triclosan	Antimicrobial	Influent	52-86,200	[89]
		Effluent	10-5,370	[89]
3PBOH	Insecticide metabolite		*	
4 - methylbenzylidene camphor (4-MBC)	UV-filter	Influent	278-6,500	[146, 151]
		Effluent	42-2300	[65, 148]
17α-estradiol	Metabolite of 17β-estradiol	Influent	*	
		Effluent		

* = Data not available in the literature